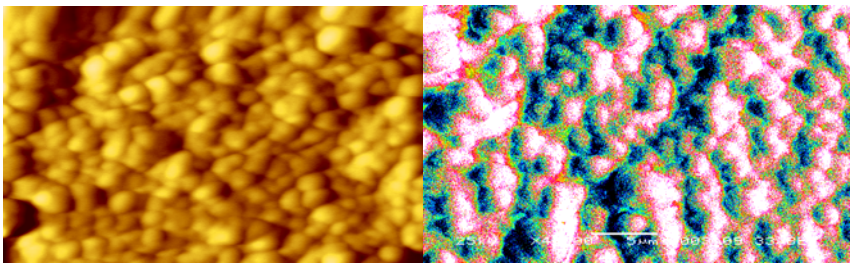
SONOELECTROCHEMICAL SYNTHESIS OF ULTRA-FINE COPPER DEPOSITS AT AMBIENT AND SUB-AMBIENT TEMPERATURES



A THESIS SUBMITTED IN PARTIAL FULFILLMENT
OF
THE REQUIREMENT FOR THE DEGREE OF

Master of Technology
in
Metallurgical and Materials Engineering

By
Ram Narayan Chauhan

Department of Metallurgical and Materials Engineering
National Institute of Technology
Rourkela
2007

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Under the guidance and supervision of

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and
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Department of Metallurgical and Materials Engineering

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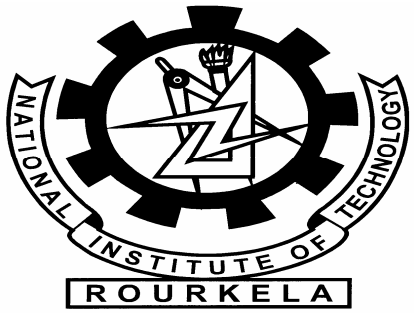

National Institute of Technology
Rourkela

CERTIFICATE

This is to certify that the thesis entitled, "**Sonoelectrochemical synthesis of ultrafine copper deposits at ambient and sub-ambient temperatures**" submitted by Mr. Ram Narayan Chauhan in partial fulfillment of the requirements for the award of Master of Technology Degree in **Metallurgical and Materials Engineering** at the National Institute of Technology, Rourkela (Deemed University) is an authentic work carried out by him under our supervision and guidance. To the best of our knowledge, the matter embodied in the thesis has not been submitted to any other University / Institute for the award of any Degree or Diploma.

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ABSTRACT

There is quiet revolution going on, and its name is nanotechnology. Without much fanfare, a host of innovations are coming our way. Use of electrochemistry, the solid/liquid interface science, in nanoscience and nanotechnology may range from nanosystems, to nanosynthesis, to nanocharacterisation. The characteristic reaction may be ion transfer reaction (ITR) or electron transfer reaction (ETR).The nanoscale electrochemistry covering from metallic and semiconductor based nanoparticles,nanoarrays,nanotubes,nanopits, to self assembled molecule monolayers i.e. bioelectrochemical systems with redox metalloprotein or DNA based molecules, has began to unravel the complexities of these systems. Electrochemistry is a suitable method for coupling particles activity to external circuitry. It has been successfully used in investigating the effects and kinetics of charge transfer at Q-dots using scanning electrochemical microscopy (SECM), by controlled transport reactions. Electrochemical processes i.e. reaction at solid/ liquid interface controlled by an externally applied voltage, are increasingly involved in nanostructured fabrication as a relatively inexpensive superior quality products, easy to handle and a reliable tool. Electroplating offers novel routes to nanosized materials via free, arrested and templated electrodeposition .As electrochemistry complements techniques under ultra high vacuum (UHV), scanning tunneling microscopy (STM) and atomic force microscopy (AFM) have taken the lead in exploring possible routes to nanostructure fabrication. Sonoelectrochemistry, ultrasound with electrochemistry is the rupture and formation of transient cavitation bubbles gives a large number of tiny regions of ultra high pressure and temperature which are known as hot spot. This may lead to a number of alterations in the electrochemical reaction kinetics and products formed. The rupture of bubble in the electrolyte/homogeneous medium produces shear forces, a general improvement of hydrodynamics and movement of species. The ion movement affects the concentration gradient at various points in the reaction profile i.e. there is a net reduction in the diffusion layer thickness and consequent switching of kinetic regimes with effect on mechanism and reaction products .Hence the limitation of ion depletion in conventional electrochemistry may be overcome and due to the high availability of nucleation sites, the

kinetics of reaction increases which may lead to form still further finer products in the nano range. Upon collapse of bubbles near the metal/electrolyte interface formation of microstream jetting obviates fouling problems and also alter the nature of coatings. This phenomena helps in formation of high-melting-temperature metal nanoclusters. Another attractive effect of ultrasound, cleavage of water molecules or organic additives helps in forming intermediate reducing radicals. This behavior of sonoelectrochemistry finds of its way in arrested electroformation of nanocomposites, complex alloys. In all the above phenomena the kinetics of nucleation has been explored to some extent but the growth kinetics is a bit contradictory as ultrasound favors diffusion readily. On this context a new field, sonocryoelectrochemistry, is emerging and is yet to be explored on nanoparticle fabrication. However in this subambient atmosphere along with mass transfer charge transfer is expected to be dominating by ultrasound through increasing the capacitance of the Helmoltz double layer or so to say the potential at outer layer may be very energetic to accelerate both cathodic and anodic reactions rather the growth. Experiments were performed under both silent and sonication conditions in ambient as well as sub ambient temperatures (from 25^0C, 19.5^0C, 5^0C, 2^0C, -1^0C, -2^0C, -3^0C). The system was electrolyte of $CuSO_4$, H_2SO_4 and water, cathode – a graphite substrate, anode – pure copper plate. The deposition was done by means of a potentiostat at an overpotential of 300mV at 1mV/s. Results were characterized by X-RD, SEM, TEM, AFM, UV-Vis spectroscopy, ADSC, heating microscope and microhardness test. It was observed that with the decrease of temperature, grain size reduced from micron region to nano region at a rate of 60-80%. And at around -3^0C the deposit was unique in the context of morphology, physical appearance and properties. The melting was observed to be decreased by 400^0C and the hardness values are also in good agreement with the deposit morphology. Novelty of ultrasound assisted deposit can be clarified by the synchronized hydrogen evolution and degassing at electrode surfaces with the plasmon resonance of nanomaterials. The work needs further investigation for a better understanding and evolution of a possible mechanism of the deposits.

Chapter 1

LITERATURE SURVEY

CHAPTER 1

1. LITERATURE SURVEY

1.1.HISTORY OF NANOTECHNOLOGY:

Although nanotechnology is a relatively recent development in scientific research, the development of its central concepts happened over a longer period of time. Humans have unwittingly employed nanotechnology for thousands of years, for example in making steel and in vulcanizing rubber. Both of these processes rely on the properties of stochastically-formed atomic ensembles mere nanometers in size, and are distinguished from chemistry in that they don't rely on the properties of individual molecules. But the development of the body of concepts now subsumed under the term nanotechnology has been slower. The first mention of some of the distinguishing concepts in nanotechnology (but predating use of that name) was in 1867 by James Clerk Maxwell when he proposed as a thought experiment a tiny entity known as Maxwell's Demon able to handle individual molecules. In the 1920's, Irving Longmuir and Katharine B. Blodgett introduced the concept of a monolayer, a layer of material one molecule thick. Longmuir won a nobel Prize in chemistry for his work.

The topic of nanotechnology was again touched upon by "There's Plenty of Room at the Bottom," a talk given by physicist Richard Feynman [1]. Feynman described a process by which the ability to manipulate individual atoms and molecules might be developed, using one set of precise tools to build and operate another proportionally smaller set, so on down to the needed scale. In the course of this, he noted, scaling issues would arise from the changing magnitude of various physical phenomena: gravity would become less important, surface tension and Vander Waals attraction would become more important, etc. This basic idea appears feasible, and exponential assembly enhances it with parallelism to produce a useful quantity of end products. At the meeting, Feynman announced two challenges, and he offered a prize a $1000 for the first individuals to solve the each one. The first challenge involved the construction of a nanomotor, which, to

Feynman's surprise, was achieved by November of 1960 by William McLellan. The second challenge involved the possibility of scaling down letters small enough so as to be able to fit the entire Encyclopedia Britannica on the head of a pin; this prize was claimed in 1985 by Tom Newman [2].

In 1965 Gordon Moore observed that silicon transistors were undergoing a continual process of scaling downward, an observation which was later codified as Moore's law. Since his observation transistor minimum feature sizes have decreased from 10 micrometers to the 45-65 nm range in 2007; one minimum feature is thus roughly 180 silicon atoms long

The term "nanotechnology" was first defined by Tokyo Science University, Norio Taniguchi in a 1974 paper [3] as follows: "'Nano-technology' mainly consists of the processing of, separation, consolidation, and deformation of materials by one atom or one molecule." Since that time the definition of nanotechnology has generally been extended upward in size to include features as large as 100 nm. Additionally, the idea that nanotechnology embraces structures exhibiting quantum mechanical aspects, such as quantum dots, has been thrown into the definition. (Figure 1) presents an overview of items from the macro to the nanoscale. One can see that multiple technical disciplines of chemistry, physics, engineering, biology and others converge as we approach the lower reaches of size [4].

Also in 1974 the process of atomic layer deposition, for depositing uniform thin films one atomic layer at a time, was developed and patented by Dr. Tuomo Suntola and co-workers in Finland.

In the 1980s the idea of nanotechology as deterministic, rather than stochastic, handling of individual atoms and molecules was conceptually explored in depth by Dr. K. Eric Drexler, who promoted the technological significance of nano-scale phenomena and devices through speeches and the books [5]. Drexler's vision of nanotechnology is often called "molecular nanotechnology" (MNT) or "molecular manufacturing," and Drexler at one point proposed the term "zettatech" which never became popular.

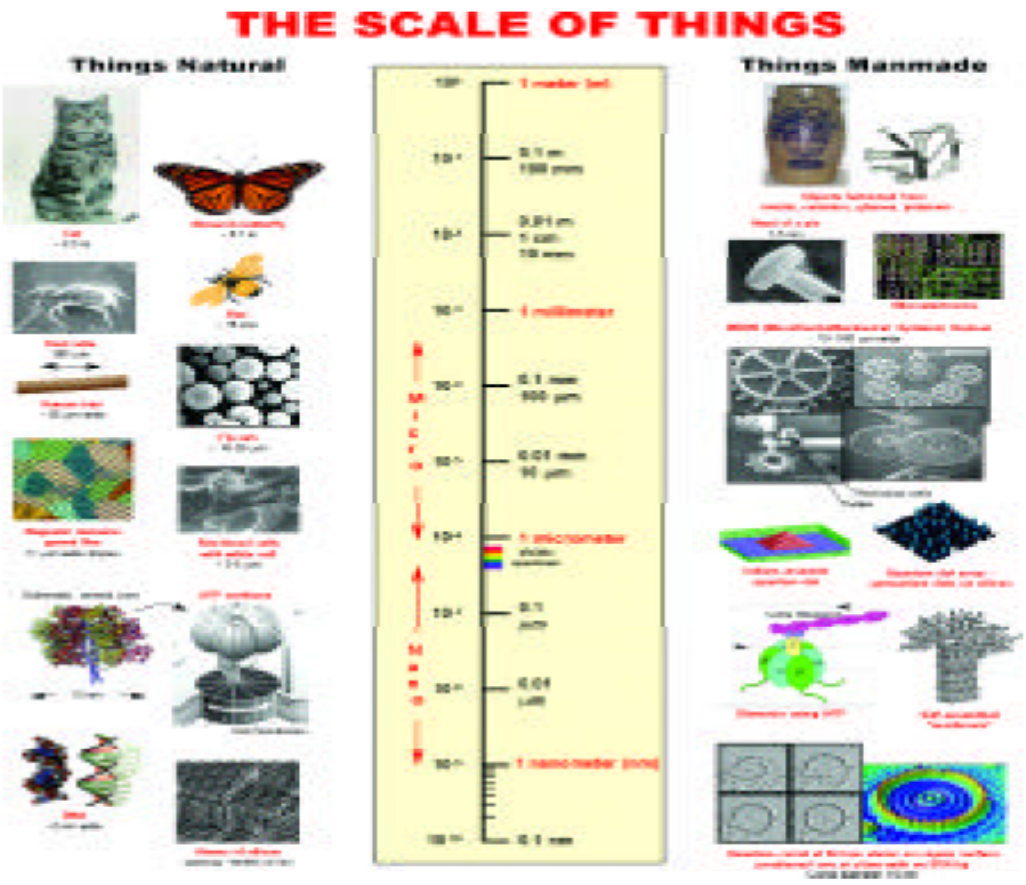

Fig.1. 1.scale of common natural and manmade items

1.2.WHAT ARE NANOMATERIALS:

Nanocrystalline materials are single- or multiphase polycrystals, the crystal size of which is of the order of a few (typically 1-10) nanometres, so that about 50 vol.% of the material consists of grain or interphase boundaries [6]. A clear picture of the structure of nanocrystalline materials is only now emerging. Whereas the earlier workers had concluded that the structure of the grain boundaries in nanocrystalline materials was quite different from that in coarse grained materials, recent studies have shown unambiguously that the structure of the grain boundaries is the same in both nanocrystalline and coarse

grained materials as proposed by the pioneer work of Gleiter [7]. For the sake of simplicity, we shall first focus on NsM formed by nm-sized crystallites. According to the shape of the crystallites, three categories of NsM may be distinguished: Layer-shaped crystallites, rod-shaped crystallites (with layer thickness or rod diameters in the order of a few nm) and NsM composed of equiaxed mn-sized crystallites. Depending on the chemical composition of the crystallites, the three categories of NsM may be grouped in four families. In the simplest case (first family, Fig. 2), all crystallites and interfacial regions have the same chemical composition. Examples of this family of NsM are semicrystalline polymers (consisting of stacked crystalline lamellae separated by noncrystalline regions; first category in Fig. 2) or NsM made up of equiaxed Cu or CaF_2 crystals (third category). NsM belonging to the second family consist of crystallites with different chemical compositions (indicated in Fig. 2 by different hatchings). Quantum well (multilayer) structures are probably the most well known examples of this type (first category). If the compositional variation occurs primarily between crystallites and the interfacial regions, the third family of NsM is obtained. In this case one type of atoms (molecules) segregates preferentially to the interfacial regions so that the structural modulation (crystals/interfaces) is coupled to the local chemical modulation. NsM consisting of nm-sized Cu crystals with Bi atoms segregated to the grain boundaries are an example of this type. (Third category). The fourth family of NsM is formed by nm-sized CrystaIlites (layers, rods, equiaxed crystallites) dispersed in a matrix of different chemical composition. Precipitation hardened alloys are examples of this group of NsM. Other examples are semicrystalline polymer blends solidified under shear. The NsM considered so far consisted mostly of crystalline components. However in addition, NsM are known in which one or all constituents are noncrystalline. For example semicrystalline polymers consist of alternating (nm thick) crystalline and non-crystalline layers. Another example are partially crystallized glasses. SpinodaIly decomposed glasses represent NsM in which all constituents are non-crystalline. Finally, crystalline or non-crystalline materials containing a high density of nm-sized voids (e.g. due to the a-particle irradiation) are NsM one component of which is a gas or vacuum.

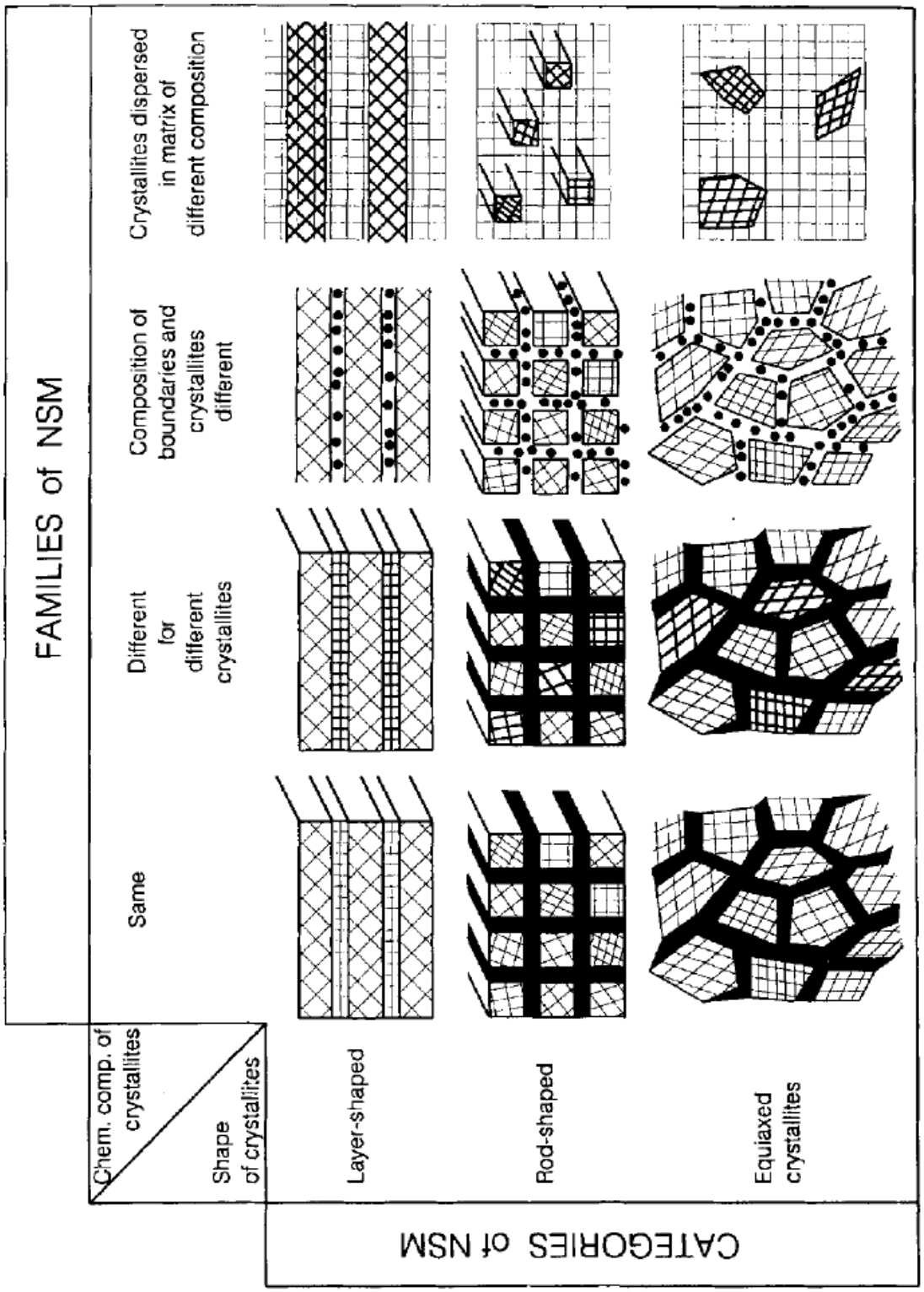

Fig 1.2.classification scheme for NsM according to their chemical composition and the dimensionality (shape) of the crystallites (structural elements) forming the NsM.

1.3.PROPERTIES OF THE INTERFACIAL MATERIALS

1.3.1. Mechanical Properties

The most widely accepted hypothesis to explain the mechanical properties in polycrystalline nanomaterials is that the strength and hardness follow the Hall-Petch relationship[8,9], increasing with smaller grain size, down to a critical grain size, dc = 10 nm, where a decrease in strength and hardness results thereafter, as depicted in Figure 1.3.

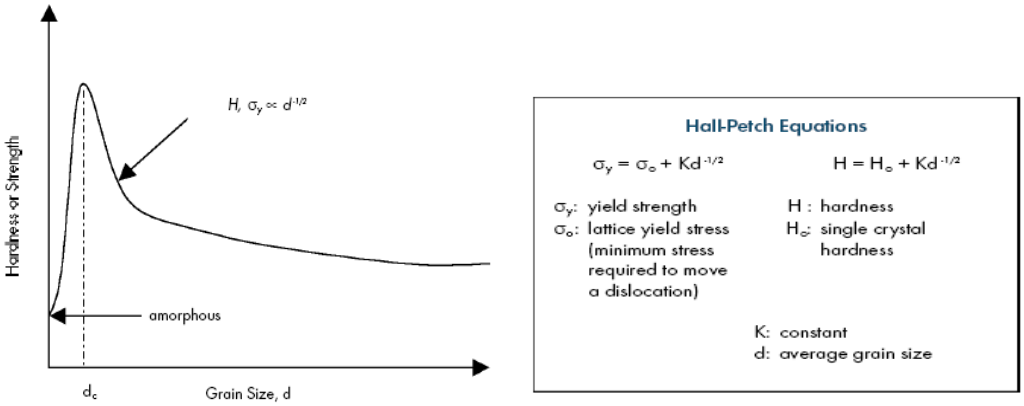

Fig.1.3. Strength/Hardness of Nanostructured Materials

The increase in strength is based upon the piling up of dislocations at g rain boundaries; i.e. by increasing the total surface area of grains, the dislocation density increases and in turn increases strength [10]. However, pileups cannot occur when the grain size is less than the dislocation spacing in the pileup; and so the Hall-Petch relationship will no longer be valid on this scale. The strength of nanoscale-thickness, multi-layered materials also follows the Hall- Petch relationship, replacing grain size with layer thickness. By decreasing grain size, the grain boundary volume relative to the unit volume will increase. At roughly 5 nm, 50% of the volume will be grain boundaries, which may then dominate the properties observed in the material. The decrease in strength at this small end of the nanoscale may be attributed to grain boundary sliding due to the high defect density allowing fast diffusion of atoms and vacancies in the stress field [11]. Super plasticity has been observed in nanostructured metals and ceramics at about 200°C lower than microstructured materials. This creates improved formability of nanostructured

materials, which is especially important for ceramics and also used in structural applications such as steam- Generator repair, wear and corrosion resistant coatings [12].

1.3.2. Thermal Properties

The enhanced diffusivity observed in the grain boundary structure of nanostructured materials is the mechanism thought responsible for the changes in thermal properties. In metals, thermal conductivity and melting point have been observed to decrease ,such as a 27°C lower melting point for gold, 300^0C in copper[13,14,15] as shown in fig1.4. While thermal expansion coefficients have been observed to increase.

The decrease in thermal conductivity of nanostructured ceramic materials such as yttria stabilized zirconia may broaden their use as thermal barrier coatings.

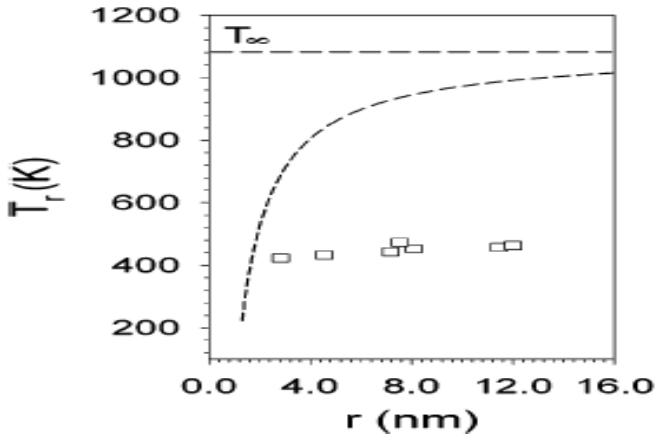

Fig1.4. Theoretical modeling of the melting temperature of copper nanoparticles as a function of particle radius based on eq 1. The parameters used for the theoretical calculation were ρ_s = 8960 and ρ_l = 8020 kg/m2, *L*= 20 500 J/Kg, and γ_s = 1.29 and γ_l = 1.11 J/m^2 .The actual temperatures used in the synthesis vs. the particle size obtained are included as square symbols.

1.3.3. Chemical Reactivity

An increased chemical activity can be obtained by the large number of atoms on the surface of nanocrystallites providing active sites for reactions. For instance,

nonstoichiometric CeO_{2-x} has a high chemical reactivity resulting from an unusually high oxygen vacancy concentration [16]. Nanostructured CeO_{2-x} has been demonstrated to offer catalytic activation for SO_2 reduction and CO oxidation at significantly lower temperatures as well as enhanced poisoning resistance (resistance to the loss of catalytic reactivity). Second classes of reactive materials are nanostructured porous materials.

Conventional porous materials such as aluminosilicates and phosphates are used for catalytic reactions and gas absorption applications, but they are limited due to their small pore sizes of less than 15 Å. Nanostructured aluminosilicates with optimized pore sizes in the range of 20–100 Å have been developed which extend their use in these markets. Similar research is being applied to the use of transition metal oxides in petrochemical production, pollution control, and pharmaceutical and fine chemical synthesis. Extending the pore sizes beyond the 20–100 Å range could provide benefits for enzyme catalysis, bioseparation and biosensing.

1.3.4. Optical Properties

The size of materials in a nano regiom can alter the wavelength of light[17,18] that is absorbed or scattered by the particulates as explained by Cecilia Noguez [19] in fig. 1.5.

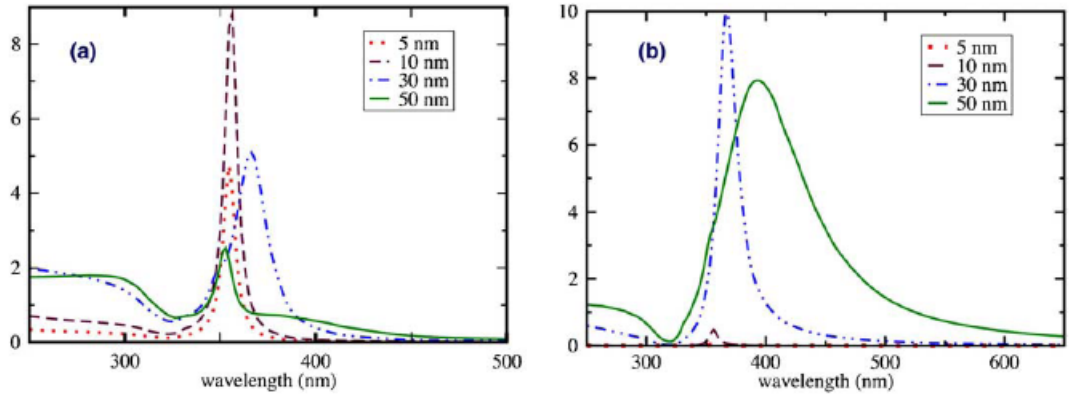

Fig1.5. (a) Absorption and (b) scattering efficiencies for spherical nanoparticles of different radii.

The quantum effect is responsible here where the discrete electron energies in the particulates determine the wavelength of light absorbed. Altering the size of a particle can

change the associated energy and wavelength of light absorbed. Cadmium selenide is one material extensively studied where crystallites of ~ 1.5 nm will appear yellow, 4 nm will appear red, and larger particles will appear black. This discovery is now being applied to sunscreen lotions using zinc oxide and Titania to filter ultraviolet radiation.

1.3.5. Electrical Properties

Quantum effects in nanomaterials have been shown to produce a non-linear dependence of electrical conductivity on electric field and can produce electron tunneling characteristics depending upon the dimensionality of nanomaterials [20] from the work of Y. Du, A.L. Ji on copper nitride thin films as shown in figure1.6.

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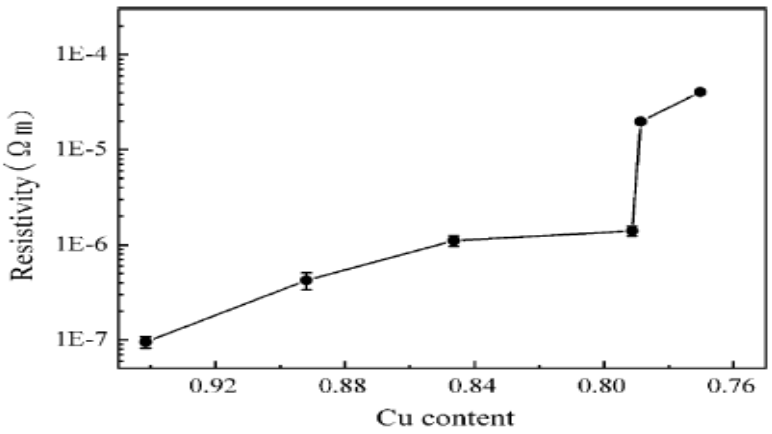


Fig1.6. Electrical resistivity of the copper nitride deposits at room temperature as a function of Cu content.

Quantum mechanical interference between separate paths an electron may take through a material can strongly enhance or suppress electrical conductivity [21]. Most of the research to date in nanostructured electronic devices comes from fabrication via lithography, but inroads are being made into molecular-level structures fabricated from chemical reactions or self assembly. For instance, quantum dots are pyramid or faceted dome-shaped clusters of atoms, typically between a few nanometers and hundreds of nanometers in diameter. They self-assemble from the deposition of a large lattice constant material onto a substrate with a small lattice constant, whereby the compressive strain in the deposited material relieves itself by causing the material to spontaneously coalesce or clump into islands on the substrate. They may be utilized as three-dimensional potential

wells if they are overgrown by a material with a larger band gap and have application potential in nanoelectronics. CNTs (the tubes formed from rolled up sheets made of carbon atoms joined in hexagonal arrays) have shown some interesting electrical properties as well. The way in which the two ends of the sheet wrap and meet can modify the longitudinal conductivity of the tube. In fact, they can be made to conduct freely like metals or behave like semiconductors. And further advancements have shown that various-sized tubes can be nested inside one another for structural or electrical performance modifications.

1.3.6. Magnetic Properties

Magnetic nanoparticles exhibit unusual behaviors resulting from the size effects and charge transfer characteristics as observed from the work of Yuqiu Qu on CoFeO4 [22] in fig.1.7.

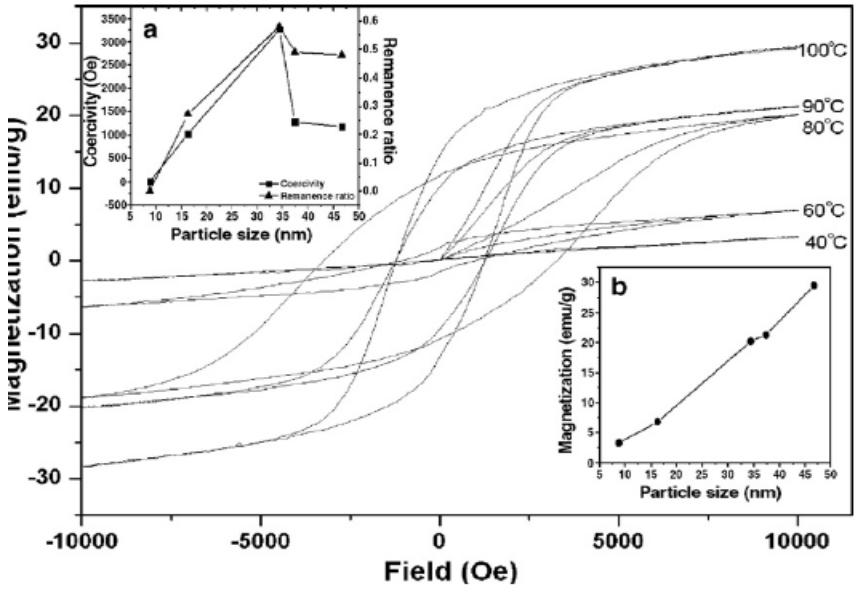


Fig1.7. Magnetization loops of $CoFe_2O_4$ nanoparticles synthesized at different temperatures. Inset a shows the variations of the coercivity and remanence ratio with particle size. Inset b shows the variation of the magnetization with particle size.

Changes seen in these materials include Giant Magneto-Resistance (GMR) in some layered composite materials and granular solids, spin valves, and spin injection in Ferro magnet/ insulator/Ferro magnet sandwich materials.

1.4.POTENTIAL APPLICATIONS:

There is a myriad of application due to miniaturization of materials from macro level to nano level.

1.4.1. Medicine

The biological and medical research communities have exploited the unique properties of nanomaterials for various applications (e.g., contrast agents for cell imaging and therapeutics for treating cancer). Terms such as biomedical nanotechnology, bionanotechnology, and nanomedicine are used to describe this hybrid field [23].

Functionalities can be added to nanomaterials by interfacing them with biological molecules or structures. The size of nanomaterials is similar to that of most biological molecules and structures; therefore, nanomaterials can be useful for both in vivo and in vitro biomedical research and applications.

Thus far, the integration of nanomaterials with biology has led to the development of diagnostic devices, contrast agents, analytical tools, physical therapy applications, and drug-delivery vehicles [23, 24, 25, 26]

1.4.1.1. Diagnostics

Nanotechnology-on-a-chip is one more dimension of lab-on-a-chip technology. Biological tests measuring the presence or activity of selected substances become quicker, more sensitive and more flexible when certain nanoscale particles are put to work as tags or labels. Magnetic nanoparticles, bound to a suitable antibody, are used to label specific molecules, structures or microorganisms. Gold nanoparticles tagged with short segments of DNA can be used for detection of genetic sequence in a sample. Multicolor optical coding for biological assays has been achieved by embedding different-sized quantum dots into polymeric microbeads. Nanopore technology for analysis of nucleic acids converts strings of nucleotides directly into electronic signatures.

1.4.1.2. Drug delivery

The overall drug consumption and side-effects can be lowered significantly by depositing the active agent in the morbid region only and in no higher dose than needed.

This highly selective approach reduces costs and human suffering. An example can be found in dendrimers and nanoporous materials. They could hold small drug molecules transporting them to the desired location. Another vision is based on small electromechanical systems: NEMS are being investigated for the active release of drugs. Some potentially important applications include cancer treatment with iron nanoparticles or gold shells...

A targeted or personalized medicine reduces the drug consumption and treatment expenses resulting in an overall societal benefit by reducing the costs to the public health system.

Nanotechnology is also opening up new opportunities in implantable delivery systems, which are often preferable to the use of injectable drugs, because the latter frequently display first-order kinetics (the blood concentration goes up rapidly, but drops exponentially over time). This rapid rise may cause difficulties with toxicity, and drug efficacy can diminish as the drug concentration falls below the targeted range.

1.4.1.3. Tissue engineering

Nanotechnology can help to reproduce or to repair damaged tissue. This so called "tissue engineering" makes use of artificially stimulated cell proliferation by using suitable nanomaterial-based scaffolds and growth factors. Tissue engineering might replace today's conventional treatments, e.g. transplantation of organs or artificial implants. On the other hand, tissue engineering is closely related to the ethical debate on human stem cells and its ethical implications.

1.4.2. Chemistry and environment

Chemical catalysis and filtration techniques are two prominent examples where nanotechnology already plays a role. The synthesis provides novel materials with tailored features and chemical properties e.g. nanoparticles with a distinct chemical surrounding (ligands) or specific optical properties. In this sense, chemistry is indeed a basic nanoscience. In a short-term perspective, chemistry will provide novel "nanomaterials" and in the long run, superior processes such as "self-assembly" will enable energy and time preserving strategies.

In a sense, all chemical synthesis can be understood in terms of nanotechnology, because of its ability to manufacture certain molecules. Thus, chemistry forms a base for nanotechnology providing tailor-made molecules, polymers etc. and furthermore clusters and nanoparticles.

1.4.2.1. Catalysis

Chemical catalysis benefits especially from nanoparticles, due to the extremely large surface to volume ratio. The application potential of nanoparticles in catalysis ranges from fuel cell to catalytic converters and photocatalytic devices. Catalysis is also important for the production of chemicals [27, 28].

1.4.2.2. Filtration

A strong influence of nanochemistry on waste-water treatment, air purification and energy storage devices is to be expected. Mechanical or chemical methods can be used for effective filtration techniques. One class of filtration techniques is based on the use of membranes with suitable hole sizes, whereby the liquid is pressed through the membrane. Nanoporous membranes are suitable for a mechanical filtration with extremely small pores smaller than 10 nm ("nanofiltration"). Nanofiltration is mainly used for the removal of ions or the separation of different fluids. On a larger scale, the membrane filtration technique is named ultrafiltration, which works down to between 10 and 100 nm. One important field of application for ultrafiltration is medical purposes as can be found in renal dialysis.

Magnetic nanoparticles offer an effective and reliable method to remove heavy metal contaminants from waste water by making use of magnetic separation techniques. Using nanoscale particles increases the efficiency to absorb the contaminants and is comparatively inexpensive compared to traditional precipitation and filtration methods.

1.4.3. Energy

The most advanced nanotechnology projects related to energy are: storage, conversion, manufacturing improvements by reducing materials and process rates, energy saving e.g. by better thermal insulation, and enhanced renewable energy sources [28, 29].

1.4.3.1. Reduction of energy consumption

A reduction of energy consumption can be reached by better insulation systems, by the use of more efficient lighting or combustion systems, and by use of lighter and stronger materials in the transportation sector. Currently used light bulbs only convert

approximately 5% of the electrical energy into light. Nanotechnological approaches like light-emitting diodes (LEDs) or quantum caged atoms (QCAs) could lead to a strong reduction of energy consumption for illumination.

1.4.3.2. Increasing the efficiency of energy production

Today's best solar cells have layers of several different semiconductors stacked together to absorb light at different energies but they still only manage to use 40 percent of the Sun's energy. Commercially available solar cells have much lower efficiencies (15-20%). Nanotechnology could help increase the efficiency of light conversion by using nanostructures with a continuum of bandgaps. The degree of efficiency of the internal combustion engine is about 30-40% at the moment. Nanotechnology could improve combustion by designing specific catalysts with maximized surface area. Scientists have recently developed tetrad-shaped nanoparticles that, when applied to a surface, instantly transform it into a solar collector.

1.4.3.3. The use of more environmentally friendly energy systems

An example for an environmentally friendly form of energy is the use of fuel cells powered by hydrogen, which is ideally produced by renewable energies. Probably the most prominent nanostructured material in fuel cells is the catalyst consisting of carbon supported noble metal particles with diameters of 1- 5 nm. Suitable materials for hydrogen storage contain a large number of small nanosized pores. Therefore many nanostructured materials like nanotubes, zeolites or alanates are under investigation.

Nanotechnology can contribute to the further reduction of combustion engine pollutants by nanoporous filters, which can clean the exhaust mechanically, by catalytic converters based on nanoscale noble metal particles or by catalytic coatings on cylinder walls and catalytic nanoparticles as additive for fuels.

1.4.3.4. Recycling of batteries

Because of the relatively low energy density of batteries the operating time is limited and a replacement or recharging is needed. The huge number of spent batteries and accumulators represent a disposal problem. The use of batteries with higher energy content or the use of rechargeable batteries or super capacitors with higher rate of recharging using nanomaterials could be helpful for the battery disposal problem.

1.4.4. Information and communication

Current high-technology production processes are based on traditional top down strategies, where nanotechnology has already been introduced silently. The critical length scale of integrated circuits is already at the nanoscale (50 nm and below) regarding the gate length of transistors in CPUs or DRAM devices or CMOS etc [30].

1.4.4.1. Novel semiconductor devices

An example of such novel devices is based on spintronics.The dependence of the resistance of a material (due to the spin of the electrons) on an external field is called magnetoresistance. This effect can be significantly amplified (GMR - Giant Magneto-Resistance) for nanosized objects, for example when two ferromagnetic layers are separated by a nonmagnetic layer, which is several nanometers thick (e.g. Co-Cu-Co). The GMR effect has led to a strong increase in the data storage density of hard disks and made the gigabyte range possible. The so called tunneling magnetoresistance (TMR) is very similar to GMR and based on the spin dependent tunneling of electrons through adjacent ferromagnetic layers. Both GMR and TMR effects can be used to create a non-volatile main memory for computers, such as the so called magnetic random access memory or MRAM.

1.4.4.2. Novel optoelectronic devices

In the modern communication technology traditional analog electrical devices are increasingly replaced by optical or optoelectronic devices due to their enormous bandwidth and capacity, respectively. Two promising examples are photonic crystals and quantum dots.

Photonic crystals are materials with a periodic variation in the refractive index with a lattice constant that is half the wavelength of the light used. They offer a selectable band gap for the propagation of a certain wavelength, thus they resemble a semiconductor, but for light or photons instead of electrons.

Quantum dots are nanoscale objects, which can be used, among many other things, for the construction of lasers. The advantage of a quantum dot laser over the traditional semiconductor laser is that their emitted wavelength depends on the diameter of the dot. Quantum dot lasers are cheaper and offer a higher beam quality than conventional laser diodes.

1.4.4.3. Displays

The production of displays with low energy consumption could be accomplished using carbon nanotubes (CNT). Carbon nanotubes can be electrically conductive and due to their small diameter of several nanometers, they can be used as field emitters with extremely high efficiency for field emission displays (FED). The principle of operation resembles that of the cathode ray tube, but on a much smaller length scale.

1.4.4.4. Nanologic

Nanoscale devices exhibit dominant nonlinearities that prevent their use as two-state devices in digital computers. The idea behind nanologic is to exploit these nonlinearities (rather than suppress them) to implement functions that correspond to mathematical sets: interval numbers, disjoint intervals, fuzzy numbers, fuzzy sets, etc. Simple nanoelectronic circuits can be designed that can represent sets and set operations, and an array of such devices constitutes a universal mathematical processor, able to solve any problem that can be expressed in set theory. Nanologic will find most value for human-meaningful problems involving uncertainty, ambiguity, error, under-specified and over-specified systems, and for approximate analysis of combinatorially intractable problems, including mathematical theorems.

1.4.4.5. Quantum computers

Entirely new approaches for computing exploit the laws of quantum mechanics for novel quantum computers, which enable the use of fast quantum algorithms.

The Quantum computer will have quantum bit memory space termed “qubit” for several computations at the same time.

1.4.5. Consumer goods

Nanotechnology is already impacting the field of consumer goods, providing products with novel functions ranging from easy-to-clean to scratch-resistant. Modern textiles are wrinkle-resistant and stain-repellent; in the mid-term clothes will become “smart”, through embedded “wearable electronics”. Already in use are different nanoparticle improved products. Especially in the field of cosmetics such novel products have a promising potential.

1.4.5.1. Foods

Nanotechnology can be applied in the production, processing, safety and packaging of food. A nanocomposite coating process could improve food packaging by

placing anti-microbial agents directly on the surface of the coated film. Nanocomposites could increase or decrease gas permeability of different fillers as is needed for different products. They can also improve the mechanical and heat-resistance properties and lower the oxygen transmission rate. Research is being performed to apply nanotechnology to the detection of chemical and biological substances for sensing biochemical changes in foods.

1.4.5.2. Household

The most prominent application of nanotechnology in the household is self-cleaning or “easy-to-clean” surfaces on ceramics or glasses. Nanoceramic particles have improved the smoothness and heat resistance of common household equipment such as the flat iron.

1.4.5.3. Optics

The first sunglasses using protective and antireflective ultrathin polymer coatings are on the market. For optics, nanotechnology also offers scratch resistant coatings based on nanocomposites. They can also help in laser surgery, as they can fix the pupil.

1.4.5.4. Textiles

The use of engineered nanofibers already makes clothes water- and stain-repellent or wrinkle-free. Textiles with a nanotechnological finish can be washed less frequently and at lower temperatures. Nanotechnology has been used to integrate tiny carbon particles membrane and guarantee full-surface protection from electrostatic charges for the wearer. A military application could be in camoflage where nanocameras mixed with nanodisplays could create an "invisibility coat", acting like the skin of a Chameleon.

1.4.5.5. Cosmetics

One field of application is in sunscreens. The traditional chemical UV protection approach suffers from its poor long-term stability. A sunscreen based on mineral nanoparticles such as titanium dioxide offer several advantages. Titanium dioxide nanoparticles have a comparable UV protection property as the bulk material, but lose the cosmetically undesirable whitening as the particle size is decreased.

1.5. Processing of nanomaterials:

The interest in the possibilities of nanostructuring materials has resulted in a variety of new methodologies for synthesizing materials with ultrafine structural are phase

domains by means of which the creation of new levels of property engineering may become possible through the sophisticated control of scale, morphology, interaction and architecture. Generally, in synthesizing NsM from atomic or molecular precursors, one wants to be able to control a variety of microscopic aspects of the condensed ensemble.

- Size and size distribution of the constituent phases or structures (domain size).
- The compositions of the constituent phases (composition)
- Nature of the interfaces created between constituent phases and hence the nature of the interaction across the interfaces (interfaces).

The properties of NsM are determined by the interplay among these features.A number of processes are used for producing nanomaterials in bulk powders, coatings, thin films, laminates, and composites. However, there are two fundamental approaches to fabricating nanomaterials. The "bottom-up" approach represents the concept of constructing a nanomaterial from basic building blocks, such as atoms or molecules. This approach illustrates the possibility of creating exact materials – materials that are designed to have exactly the properties desired. The second approach, the "top-down" method, involves restructuring a bulk material in order to create a nanostructure.In essence, there are four generic routes to make nanoparticles [31].

1.5.1. Mechanical route

These include milling by ball mill, planetary mills, attrition mills, vibratory mills etc. The advantages of these techniques are that they are simple, require low-cost equipment and, provided that a coarse feedstock powder can be made, the powder can be processed. However, there can be difficulties such as agglomeration of the powders, broad particle size distributions, contamination from the process equipment itself, and often difficulty in getting to the very fine particle sizes with viable yields. It is commonly used for inorganic and metals, but not organic materials.

1.5.2. Form-in place

These include lithography, vacuum deposition processes such as physical vapor deposition (PVD) and chemical vapor deposition (CVD), and spray coatings. These processes are more geared to the production of nanostructured layers and coatings, but can be used to fabricate nanoparticles by scraping the deposits from the collector. However,

they tend to be quite inefficient and are generally not used for the fabrication of dry powders.

1.5.3. Gas-phase method

These include flame-pyrolysis, electro-explosion, laser ablation, high-temperature evaporation, and plasma synthesis techniques. Flame pyrolysis has been used for simple materials such as carbon black and fumed silica, and is being used in the fabrication of many more compounds. Laser ablation is capable of making almost any nanomaterials, since it utilizes a mix of physical erosion and evaporation.

1.5.4. Wet chemical route

These include precipitation techniques, sol-gels, colloidal chemistry, electrochemistry, Sonoelectrochemistry etc. Essentially; solutions of different ions are mixed in well-defined quantities and under controlled conditions of heat, temperature, and pressure to promote the formation of insoluble compounds, which precipitate out of solution. These precipitates are then collected through filtering and/or spray drying to produce a dry powder. The advantages of these wet chemical processes are that a large variety of compounds can be fabricated, including inorganics, organics, and also some metals, in essentially cheap equipment and significant quantities. Another important factor is the ability to control particle size closely and to produce highly monodisperse materials. However there are limitations with the range of compounds possible, bound water molecules can be a problem, and, especially for sol-gel processing, the yields can be quite low.

It is worth exploring each of these basic routes, as the resultant materials can have significantly different properties, depending on the route chosen to fabricate them, and some routes are more aligned with the fabrication of certain classes of materials.

1.6. Electrochemistry towards nanofabrication:

There is quiet revolution going on, and its name is nanotechnology. Without much fanfare, a host of innovations are coming our way. Use of electrochemistry, the solid/liquid interface science, in nanoscience and nanotechnology may range from nanosystems, to nanosynthesis, to nano characterization. The characteristic reaction may be ion transfer reaction (ITR) or electron transfer reaction (ETR).The nanoscale electrochemistry covering from metallic and semiconductor based nanoparticles ,nanoarrays,nanotubes,nanopits [32],

to self assembled molecule monolayers i.e. bioelectrochemical systems with redox metalloprotein or DNA based molecules [33], has began to unravel the complexities of these systems. Electrochemistry is a suitable method for coupling particles activity to external circuitry. It has been successfully used in investigating the effects and kinetics of charge transfer [34] at Q-dots using scanning electrochemical microscopy (SECM), by controlled transport reactions. Electrocrystallization processes occurring at electrochemical solid/liquid interfaces have for a long time attracted the interest of many researchers from both fundamental and applied viewpoints. Electrocrystallization not only represents an interesting case of phase formation and crystal growth but is also a powerful method for various technological applications because the driving force of the process can be easily controlled by the current density and the electrode potential [35]. Over the past decade, electrodeposited nanostrutures have advanced rapidly to commercial application because of the following factors, i) an established industrial infrastructure, ii) relatively low cost of application where by nanomaterials can be produced by simple modification of bath chemistry and electrical; parameters used in current plating and electroforming operations, iii) the capability in a single step process to produce metals, alloys and metal-matrix composites in various forms, iv) the ability to produce fully dense nanostrtures free of extraneous porosity. Important processing parameters include bath composition, pH, temperature, overpotential, bath additives, substrate types etc.

1.6.1. Factors affecting nucleation and growth phenomena at the electrode surface:

In view of the industrial importance of the electrodeposition of metals, the influence of various factors on the physical appearance of the deposits has been the subject of much investigation. It is generally agreed that electrodeposited metals are crystalline, and the external appearance depends mainly on the rate at which the crystals grow and on the rate of the formation of fresh nuclei. If the conditions are such as to favor the rapid formation of crystal nuclei, the deposit will be fine grained; if the tendency is for the nuclei to grow rapidly, however, relatively large crystals will form and the deposit becomes rough in appearance [36].

1.6.1.1. Current Density

At low current densities the discharge of ions occurs slowly, and so the rate of the growth of the nuclei should exceed the rate at which new ones form; the deposits obtained

under these conditions should be coarsely crystalline. As the current density is raised the rate of formation of nuclei will be greater and the deposit will become finer-grained. At very high currents the solution in the vicinity of the cathode will be depleted in the ions required for discharge, and, as a result, the crystals will tend to grow outwards towards regions of higher concentration; the deposit then consists of "trees," nodules or protruding crystals. If the current density exceeds the limiting value for the given electrolyte, hydrogen will be evolved at the same time as the metal is deposited; bubble formation often interferes with crystal growth, and porous and spongy deposits may be obtained. The discharge of hydrogen ions frequently causes the solution in the vicinity of the cathode to become alkaline, with the consequent precipitation of hydrous oxides or basic salts; if these are included in the deposit, the latter will be fine-grained and dark in appearance.

1.6.1.2. Concentration of Electrolyte

The effects of the electrolyte concentration and of current density are to a great extent complementary by increasing the concentration or by agitating the solution, higher current densities can be used before coarse deposits are formed, or before hydrogen evolution occurs with its accompanying spongy or dark deposits. The influence of concentration on the rate of nucleus formation is uncertain; since increase of concentration tends to give firm, adherent deposits, some workers have expressed the opinion that the presence of the large number of ions in a concentrated solution favors the formation of fresh nuclei. Certain experiments, however ,indicate that the rate of formation of nuclei is actually decreased by increasing concentration, but the improvement in the deposit is due to an increase in the rate of growth of crystals over the cathode surface, combined with a decrease in the rate of growth in a perpendicular direction.

1.6.1.3. Temperature

Increase of temperature has two effects which oppose one another: in the first place, diffusion is favored, so that the formation of rough or spongy deposits at relatively high current densities is inhibited. On the other hand, the rate of crystal growth, favoring coarse deposits, is increased. Further, increase of temperature decreases hydrogen overvoltage, and so facilitates the evolution of the gas, as well as the precipitation of basic salts. At moderate temperatures the first of the three aforementioned factors predominates, so that the deposits are improved, but at higher temperatures deterioration is observed. The

low temperature is important for systems in which undesirable interdiffusion between adjacent layers or structures can occur, whereas the high selectivity of electrocrystallization processes allows uniform modification of surfaces and structures with complicated profiles.

1.6.1.4. Colloid Matter

In many instances, e.g., lead from acetate solution or silver from silver nitrate, the metal normally deposits on the cathode in the form of relatively large crystals, but the presence of very small amounts of colloidal matter, or of certain organic compound, often results in the production of a smooth, fine-grained and microcrystalline deposit[37]. The action of any particular substance is often specific and depends on the nature of the metal and the electrolyte. The addition agents are generally surface-active substances and they are probably adsorbed on the crystal nuclei, thus preventing their growth; the discharge ions are consequently compelled to start new nuclei and the result is that the deposit is fine-grained whereas it might otherwise have been appreciably crystalline. The deposits obtained in the presence of an addition agent have been found to contain a certain proportion of the latter, in agreement with the view that the added substance is observed.

1.6.1.5. Electrolyte

The nature of the anion often has a very important influence on the physical form of the deposited metal; for example lead from lead nitrate solution is rough, but smooth deposits are obtained from silicofluride and borofluride solution. The valence state of the metal may affect the nature of the deposit; thus from plumbic solutions lead is deposited in spongy form whereas relatively large crystals are formed in plumbus solutions. In an analogous manner, smooth deposits of tin are obtained from stannate baths, but from stannite solutions the deposits are of poor quality. The difference in the behavior of different electrolytes is sometimes due to the possibility of the formation of colloidal matter which serves to give a fine-grained deposits; this may be the case in the deposition of lead from silicofluride and borofluride solutions where a certain amount of colloidal hydrous silica or borrontrioxide may be formed by hydrolysis.

1.6.1.6. Basis Metal

Although the external form of a deposited metal is rarely affected by the basis metal used as the cathode, there is ample evidence that the latter has some effect on the

crystal growth. It is apparent that in many instances the general orientation of the crystals, at least in the first layers of the deposit, is a continuation of that in the basis metal.

1.6.2. Throwing Power

The property of solution by virtue of which a relatively uniform deposit of metal may be obtained on a cathode of irregular shape; is known as the throwing power. The problem of the causes of good or bad throwing power is very complex and is not at all clearly understood. It appears, from a theoretical standpoint, that throwing power should be influenced by (a) the rate of increase of cathode potential with current density, and (b) the conductance of the solution. If preferential deposition should take place at any part of the cathode, the effective current density will be higher here than on the remainder of the cathode; if this higher density requires a much increased potential, there will be a tendency for the current density to be automatically reduced at the part under consideration. In other words, a cathode potential-current density curve with a marked slop should favor uniform current distribution and so should give good throwing power. This appears to be true in certain cases, but there are other important factors to be considered, for a solution of argentocyanide containing excess free cyanide appears to have excellent throwing power, although the polarization does not increase markedly with increasing current density. In general, the addition of colloidal matter improves the throwing power of a solution, but increase of temperature and agitation has the opposite effect.

If the conductance of the electrolyte is low, the current lines will tend to concentrate on the parts of the cathode nearest the anode and the throwing power will be bad. With a solution of good conductance, however, there will be no particular preference. The conductance of an electrolytic bath is generally so good, however, that there is no noticeable influence on the throwing power.

1.6.3. Simultaneous Discharge of Cation

If a solution contains two cations, there is a possibility that simultaneous discharge may occurs: this problem is not only of interest in connection with the electrodeposition of alloys, but it is important in the deposition of single metals, since aqueous solutions always contain hydrogen ions. Were it not for a variety of complicating factors, such as the influence of one metal on the deposition potential of the other, the situation would, in principle, be relatively simple; provided the discharge (reduction)

potentials of the two ions were the same, simultaneous deposition would occur. For example the reversible potential of a metal A in a solution of its ions of activity $a_A^{+, i.e}$., of the electrode A, A^+ would be given by

$$E= E^0_A- (RT/Z_AF) \ln a_A^+,$$

And the theoretical discharge potential $E_{dis.}$ is equal to –E, i.e.,

$$E_{dis.} = -E^0_A+ (RT/Z_AF) \ln a_A^+$$

In order to obtain the actual discharge potential it is necessary to include the overvoltage $\omega_{A,}$ and so it follows that

$$E_{dis.} = -E^0_A -\omega_A + (RT/Z_AF) \ln a_A^+$$

If the solution contains two cations, one of which may be the hydrogen ion, then provided there is no interaction in solution or in the deposit, simultaneous deposition will occur when the two discharge potentias, e.g, of A and B, become equal; that is, when

$$-E^0_A -\omega_A + (RT/Z_AF) \ln a_A^+ = -E^0_B -\omega_B + (RT/Z_BF) \ln a_B^+$$

The subject of simultaneous discharge may be divided into two aspects: first, when it is desired to deposit two metals simultaneously, e.g., in alloy deposition, and second, when simultaneous deposition is to be avoided, e.g., in electro-analytical work. These aspects will be considered in turn.

An examination of equation of equation (1) shows that there are, in general, three ways in which the discharge potentials of two cations may be brought together (1)if the standard potentials are approximately equal and the overvoltage are small(2)if the standard potentials are different, but the overvoltages vary sufficiently to compensate for this difference; and(3)if the differences in reversible potential and overvoltage are compensated for by differences in the activities of the ions.

1.6.4. Overvoltage

Although the decomposition voltage of an aqueous solution of an acid or base is about 1.7 volts with smooth platinum electrodes, the value is different if other metals are employed as the electrode material. This dependence of the decomposition voltage and discharge potential on the nature of the electrode had been known for many years, but it was not studied in a systematic manner until 1899 when Caspari observed the potentials at which visible evolution of hydrogen and oxygen gases occurred at cathodes and anodes, respectively, of a number of different metals. The difference between the potential of the

electrode when gas evolution was actually observed and the theoretical reversible value for the same solution was called the overvoltage.It is not certain if the point at which visible evolution of hydrogen or oxygen gas in form of bubbles has any theoretical significance, although the potential corresponds approximately to that ,where appreciable current begins to flow: nevertheless the results are of practical interest in connection with the possibility of hydrogen evolution as an alternative process in electrolytic reduction and metal deposition. In order to distinguish between the over voltage corresponding to the commencement of gas evolution and the value at a definite current density, the former has been referred to as the" minimum over voltage ".The adjective "minimum" is somewhat misleading, however, since hydrogen evolution is possible at lower over voltage; the term "bubble overvoltage "will therefore, be employed as it gives a more exact description of what is measured.

The bubble overvoltages for hydrogen are almost independent of PH, although there is sometimes a small decrease in alkaline solution. Anodic overvoltages are even less reproducible than are those accompanying hydrogen evolution, and there is little definite information concerning the influence of PH; it is probable, however, from the fact that the decomposition voltages of acid and alkaline solutions are the same that the oxygen overvoltage,at least for platinum is approximately constant. Both cathodic and anodic overvoltages decrease with increasing temperature; the exact extent is not known, but it is generally about 2 millivolts per degree. Sufficient general information has now been given to permit a consideration of theory of overvoltage, and to allow an attempt to be made to elucidate the nature of the slow process involved in the discharge of hydrogen ions. The stages in the reaction at cathode in aqueous solution are as follows:(1) transfer and diffusion of H_3O^+ ions to the electrode layer;(2) transfer of these ions, or protons, to the electrode;(3) neutralization of the charge of these ions or protons by electrons;(4) Combination of the resulting hydrogen atoms to form molecules; and (5) evolution of the hydrogen molecules as bubbles of gas.

1.7. Sonoelectrochemistry a novel route:

Electrochemistry is an old discipline. Faraday worked through the 1830's, and Kolbe reported his electroorganic synthetic reaction in 1849. The vibration of electrochemical cells is likewise a concept of some standing, and Moriguchi reported the improvement of

water electrolysis by insonation in 1934. Thereafter, sporadic reports can be found on sonoelectrochemistry, although this term was not used as a descriptor until more recently. This period included an extensive study by Yeager upon the physicochemical parameters of ionic solutions. Ultrasound was also shown to affect metal electrodeposition with benefit to the quality of the deposit, its adhesion and morphology, and also the diminution of brighteners and other additives needed in silent systems, such as the toxic molecule thiourea [38]. Other effects of ultrasound on phase phenomena included emulsification to facilitate the electrolytic dechlorination of polychlorinated aromatic molecules. Ultrasound (which can affect *per se* the RMM of polymers) also influenced a series of electro initiated polymerizations, and separately had been shown to affect the electrogeneration of organochalcogenide species. At this point, in the late 1980s, we produced our first paper from Coventry showing a mechanistic switch in an electroorganic synthetic reaction, namely the Kolbe electro oxidation of cyclohexanecarboxylate in methanol. Here the preponderance of the one-electron per molecule dimer bicyclohexyl in the silent system was converted into two-electron per molecule products such as cyclohexyl methyl ether and cyclohexene in the insonated system. Our paper closely followed one reporting the effect of ultrasound on electrodeposition of the conducting polymer polythiophene, and somewhat predated the first in a series of reports on various organic sonoelectrochemical systems by Nonaka, Atobe . These workers found a reverse mechanistic switch in the electroreduction of carbonyl compounds, from the two-electron-per molecule monomeric alcohol in the silent system, to the one-electron per molecule dimeric pinacol under insonation. Since then, interest in sonoelectrochemistry has grown considerably, with some 100 papers published last year using this keyword. This is a result of the general enhancement in both electrochemical and sonochemical equipment and methodology, allowing a wider range of experiments and a greater understanding of phenomena. Comprehensive studies have been made by several groups including Nonaka and Atobe at Tokyo, and particularly by RG Compton *et al.* at Oxford, who have produced a very significant proportion of recent publications in the field. There have been a number of reviews to which the reader is directed for a more thorough account of the history and of recent developments. It must also be noted that while the underpinning funding for these studies has come from a variety of sources, including National Research Councils and their

equivalents, the considerable European effort into sonoelectrochemistry is due to specific support by the European Union under a series of overlapping initiatives into 'Non-Classical Methodologies' in chemistry. Thus, Coventry, Oxford, Brussels and Coimbra Universities collaborated in a Human Capital and Mobility Network in sonoelectrochemistry as part of the EU Fourth Framework initiative, which included the COST D6 programme 'Chemical Reactions and Processes under Extreme and Non-Classic Conditions', and currently Coventry, Oxford, Brussels, Coimbra, Alicante and Rostock Universities comprise a Fifth Framework COST D10 Working Group on sonoelectrochemistry in the programme 'Innovative Methods and Techniques for Chemical Transformations'.

Sound comprises longitudinal waves that cause compression and rarefaction cycles as they pass through a medium. Audible sound covers the frequency range from approximately 16 Hz to 16 kHz, and ultrasonic frequencies are higher than this. Generally the frequency region just above hearing is called 'power' ultrasound (20 – 100 kHz) and this where ultrasonic cleaning baths and commercial plastic welding apparatus operate, while frequencies near and above 1 MHz are used for diagnostics, medical scans and other analytical applications. The effects of ultrasound in a liquid are to cause 'acoustic streaming' and/or the formation of cavitation bubbles, depending upon the parameters of ultrasonic power, frequency, sonic source characteristics, and solution phenomena such as viscosity, volatility, and the presence of dissolved gases or other nucleation sites[38,39]. Calculations have shown that the formation and decay of cavitation bubbles involve transient extremes of temperature (5000-25,000k) [40] and pressure, due to hot-spot mechanism, because the collapse occurs in less than nanosecond[41,42,43] and the bubbles can form micro jets that impinge towards a surface. These are responsible for the cleaning effect of a laboratory ultrasonic cleaning bath and the observation of neat holes punched through a sheet of aluminium cooking foil held vertically in such a bath. However, other phenomena occur, and sonoluminescence, the weak evolution of light particularly from insonated aqueous systems, is of fundamental physicochemical significance. The placing of a heterogeneous solid interface, the electrode surface, into a liquid medium under insonation offers a number of potential effects, particularly given the range of electrochemical parameters that may be varied in addition to ultrasonic ones. Thus, solvent, electrolyte, electrode material, cell geometry and geometric disposition of the electrode,

electrode potential and/or dynamic modulation of potential or current density (for example by pulsing or cyclic scanning), and the presence of quenching or trapping agents, may all be varied within a single system to affect the course of electrochemical reaction of the substrate molecule for resulting nanosized particles. This gives a great deal of experimental flexibility in sonoelectrochemical methodology. A number of possible effects of ultrasound upon an electrochemical system may be predicted:

- A general improvement of hydrodynamics and movement of species;
- The alteration of concentration gradients at various points in the reaction profile, and consequent switching of kinetic regimes with effect on mechanism and reaction products;
- A cleaning and abrading effect upon an electrode surface, thus obviating fouling problems, or else altering the nature of coatings that manage to form;
- Sonochemically-induced reactions of intermediate species that have been generated electrochemically;
- The sonochemical formation of species that react electrochemically in conditions where the silent system is electro inactive.

In all the above phenomena the kinetics of nucleation has been explored to some extent but the growth kinetics is a bit contradictory as ultrasound favors diffusion readily. On this context a new field, sonocryoelectrochemistry [44,45,46] is emerging and is yet to be explored on nanoparticle fabrication. However in this sub-ambient atmosphere along with mass transfer charge transfer is expected to be dominating by ultrasound through increasing the capacitance of the Helmoltz double layer or so to say the potential at outer layer may be very energetic to accelerate both cathodic and anodic reactions rather the growth.

1.8. Objectives:

- Synthesis of ultra fine/nano copper deposits through sonoelectrochemical route at ambient and sub-ambient temperatures.

- Characterization of the above deposits by X-RD, TEM, SEM, UV-Vis spectroscopy, AFM, ADSC

- Study of properties like microhardness and melting of the fabricated structure by microhardness tester and heating microscope.

Chapter 2

EXPERIMENTAL SECTION

CHAPTER2

2. EXPERIMENTAL SECTION

2.1. INSTRUMENTATION

Electrochemical studies or experiments were done with EG&G 273 potentiostat system and three electrode electrochemical cell. The working electrode was a Cu-plate; the counter electrode was a rough graphite plate and Ag/AgCl saturated calomel electrode (SCE) worked as reference electrode. Before each scan and subsequent experiments, electrodes were polished, washed and dried properly. For sonoelectrochemical experiment ultrasonic vibrator of frequency (20 KHz) was used, which was positioned just below the electrochemical cell. The arrangement is shown in figure 2.1.

a b

fig. 2.1. Experimental Set up (a) ambient condition (b) sub-ambient condition

For low temperature electrodeposition and low temperature sonoelectrochemical studies were done with the electrochemical cell placed in refrigerator which temperature varies from room temperature to -20^0C.The temperature of electrolyte was measured with digital thermometer.

2.2. SYNTHESIS

Electrodeposition is used as a route to fabricate copper nanoparticles. The deposition was commenced in potentiostatic mode. The electrolyte used was a mixture of $CuSO_4$ (Cu = 10g/l), H_2SO_4 (40g/l) and rest water at various temperatures including ambient to sub-ambient temperatures, 19.6^0C, 5^0C, 2^0C,-1^0C,-2^0C,-3^0C. Doubly distilled water and analytical grade chemicals were used for the electrodeposition of copper. Before each scan and subsequent

experiments, the electrodes were polished. The potential range applied for the deposition varied between 0.1V to 0.6V with reference to SCE at a scanning arte of 1mV/s. The dissolution of copper plate and deposition on graphite electrode has taken place in the working potential range for each respective temperatures (25^0C, 19.6^0C, 5^0C, 2^0C,-1^0C,-2^0C,-3^0C). During electrodeposition the electrolytic solution was not stirred.

Sonoelectrodeposition is used as a recent technique to fabricate Cu nanoparticles in which an additional instrument such as ultrasound vibrator of frequency 20 KHz was used to agitate the solution to increase the reaction rate of formation of copper nanoparticles at respective temperatures.

2.3. CHARACTERIZATION TECHNIQUES

Several techniques have been used to characterize the electrodeposits and sonoelectrodeposits at various temperatures (25^0C, 19.5^0C, 5^0C, 2^0C,-1^0C,-2^0C,-3.1^0C,-5.6^0C).X-ray diffraction (XRD) patterns of the electrodeposits and sonoelectrodeposits were recorded with an Philips X-ray diffractometer using CuKά radiation(λ=1.54Å). JEOL scanning electron microscope (SEM) at low acceleration voltages, transmission electron microscope (TEM) & atomic force microscope (AFM) were employed to examine the morphology, particle size and microstructure of the electrodeposits and sonoelectrodeposits at the various temperatures. The chemical composition/purity of the electrodeposits and sonoelectrodeposits was determined by energy dispersive spectroscopy (EDS) analysis. To support the result obtained by the above methods UV-visible spectroscopy was employed. The sample for the spectroscopy measurement was prepared by agitating the deposit under sonication in ethanol for about 3hours. The measurement was done with the reference sample of ethanol. Melting property was studied by a Leica heating microscope (0-1700^0C). A new and innovative sample preparation method was followed for sample preparation. The electrodeposited sample was smoothly cut into the required pellet size and was kept inside the microscope. The result was compared with a pellet sample of pure copper powder. Though microhardness study is not appropriate for nanomaterials but due to the very novel type of deposit, the study shows some relevance with the deposit. This was commenced in a Leitz microhardness tester.

Chapter 3

RESULTS AND DISCUSSION

CHAPTER3

3. **RESULTS AND DISCUSSION**

3.1. X-RD ANALYSIS

The X-RD patterns of the sample synthesized at different raction temperatures both at silent and sonication conditions are shown in figs 3.1. and 3.2. respectively.

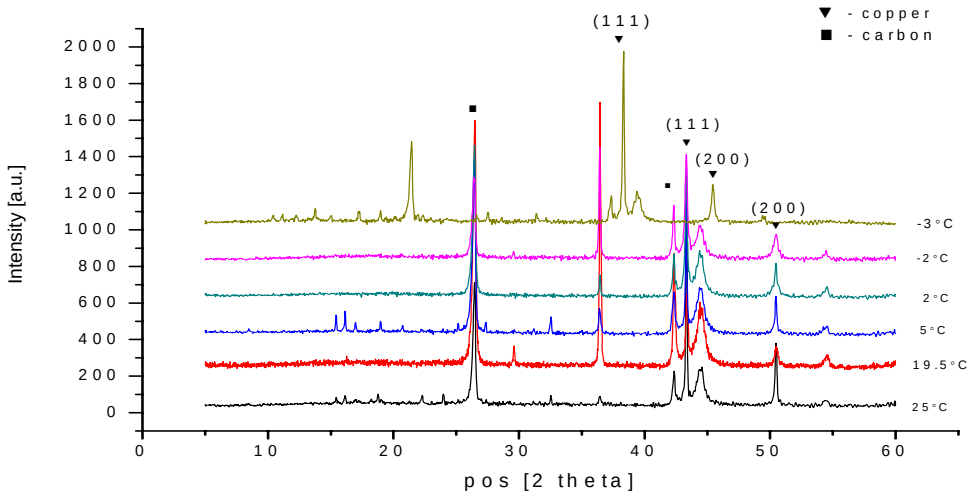


Fig.3.1. XRD patterns of ultra-fine copper electrodeposits at various temperatures (from ambient to sub-ambient temperatures).

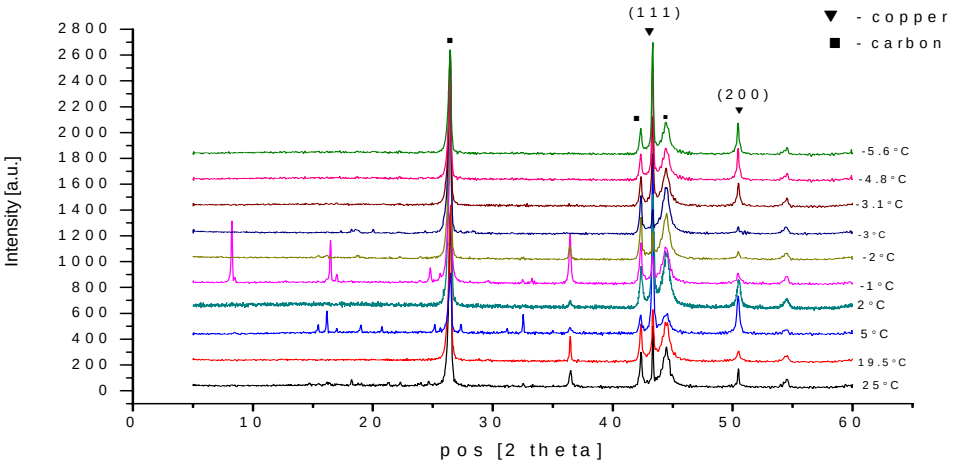


Fig.3.2. XRD patterns of ultra-fine copper sonoelectrodeposits at various temperatures (from ambient to sub-ambient temperatures).

The X-RD pattern reveals that the peaks correspond to characteristic peaks of cubic copper lattice (JCPDS file no.04-0836) of (111) and (200) planes. Along with copper there are some peaks of carbon (due to the substrate material), sulphur (from the electrolyte) peaks are also there. The pattern also reveals that the decrease in temperature, intensity decreases where as broadening increases though not in regular fashion. The broadening of peaks can be attributed to small particle size and strain of crystalline materials. Using the method developed by Williamson and Hall [47], the contributions of the particle size and strain to be observed X-ray line broadening, β , are considered to be additive.

$$\beta_{\text{total}} = \beta_{\text{particle size}} + \beta_{\text{strain}}$$

The contribution of broadening due to small particle size is given by Scherrer equation while the broadening due to strain is represented by differentiation of Bragg's law.

$$\beta_{\text{total}} = \frac{0.94\lambda}{t\cos\theta} + 4\tan\theta(\Delta d/d) \qquad (2)$$

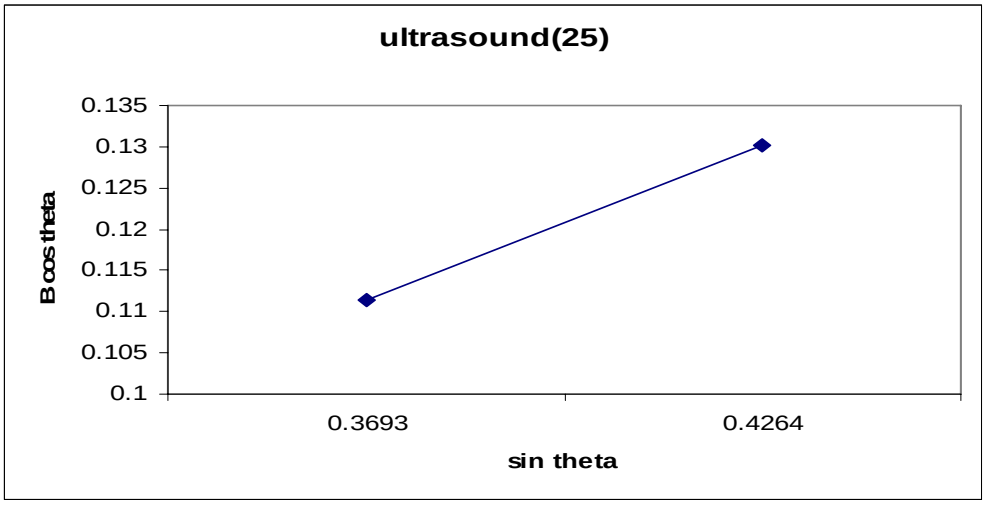


Fig.3.3. Williamson–Hall plot for ultra-fine copper sonoelectrodeposits at ambient temperature from X-ray diffraction pattern.

The total broadening (β_{total}) is the measured FWHM total in radians, corrected for instrumental broadening. The X-ray wavelength of the source (CuKa0.154nm) is given by

λ, *t* is the particle size, and Δ*d*/*d* represents the strain. Multiplying both sides of Eq.(2) by cos θ gives the final form,

$$\beta_{total} \cos\theta = \frac{0.94\lambda}{t} + 4 \sin\theta(\Delta d/d)$$

which is used to calculate the particle size and strain for copper from a plot of β_{total} cos θ versus sin θ, total as shown in Fig 3.3. Using the *y*-intercept obtained from linear regression of the broadening as a function of diffraction angle, we obtained average particle size ranging from 1-14nm. The size distribution vs. temperature is shown in figs.3.4. and 3.5.for silent and sonication condition respectively. The graphs show that decrease in temperature results in decrease in grain size.

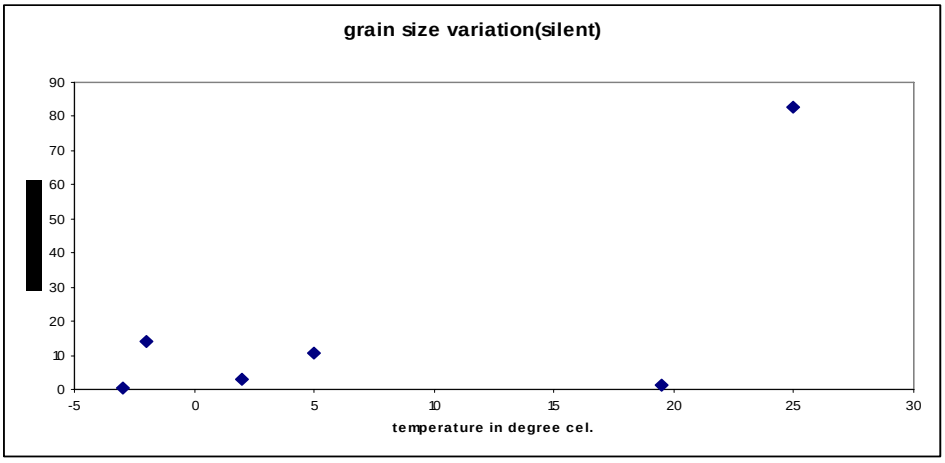


Fig.3.4.Plot of graph between grains sizes vs. temperatures for ultra-fine copper deposits during silent condition

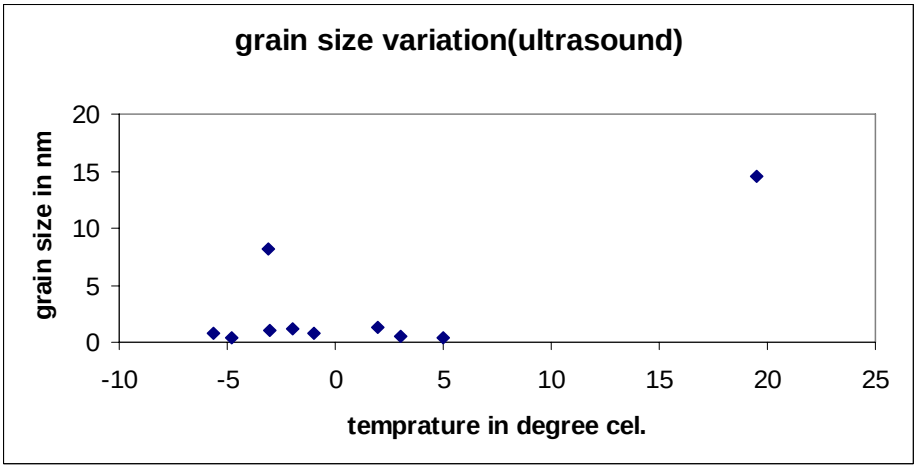


Fig.3.5. Plot of graph between grains sizes vs. temperatures for ultra-fine copper deposits during sonication.

3.2. SEM ANALYSIS

Figures 3.6. (a), (b), (c), (d) show the SEM graphs of copper electrodeposits obtained both at silent and sonication condition in ambient, sub-ambient temperatures and are compared. Both the deposits show different fashions in morphology. It is known that the formation of dendritic deposit is a main characteristic of electrodeposition at overpotentials belonging to the plateau of the limiting diffusion current density and that the induction time of a dendritic growth initiation depends on overpotential of the electrodeposition. The increase in overpotential leads to the decrease of time needed for the initiation of the dendritic growth. As the range of overpotential has been kept constant the dendritic morphology will be controlled by temperature alone.

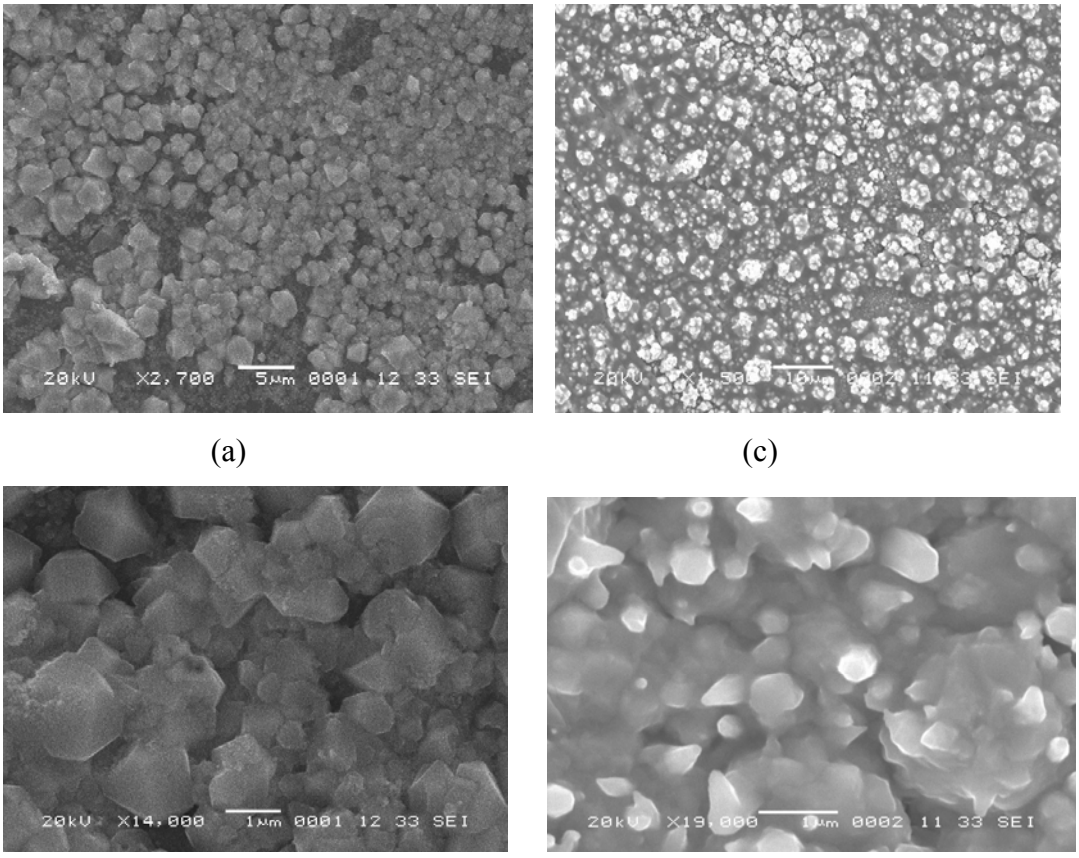
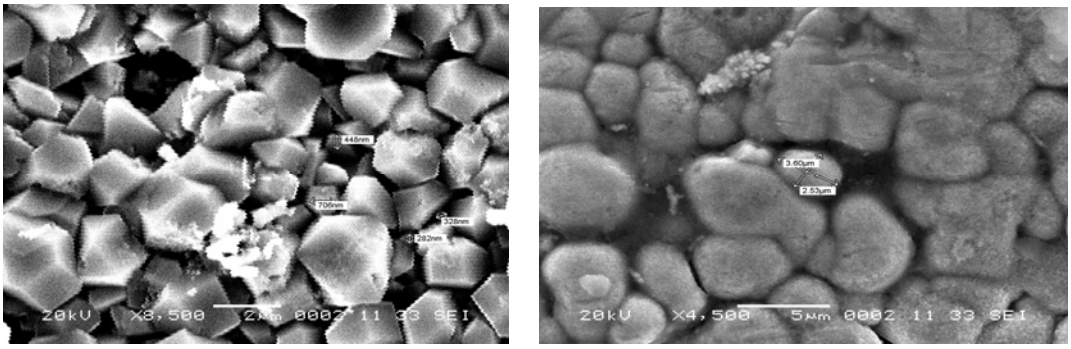


Fig.3.6. SEM micrographs of Cu electrodeposit at ambient temperature(25^0C) (a-b) silent sample (c-d) sonicated sample

The analysis of copper morphology shown in fig. reveals the difference between copper deposit at the two conditions .The deposit at ambient temperature in silent condition

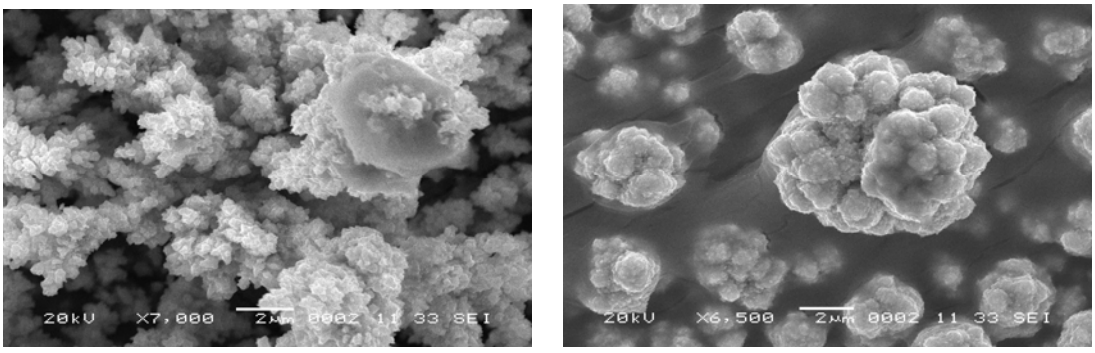
appears to be regular and granular type whereas under sonication the deposit seems to be an adherent forged layer with copper spikes. Now comparing the deposit at around 20^0C in fig.3.7 there is no remarkable change in morphology of electrodeposited copper but under sonication a dramatic change from a forged layer to and intermediate or semi sintered layer can be seen. This shows agglomeration of small clusters and the neck formation. At ambient temperature (relatively high temperature) the unique structure may be correlated with the fact that ultrasonic irradiation may lead to interparticle collision for the sintered layer. This high velocity collision localized melting or plastic deformation.



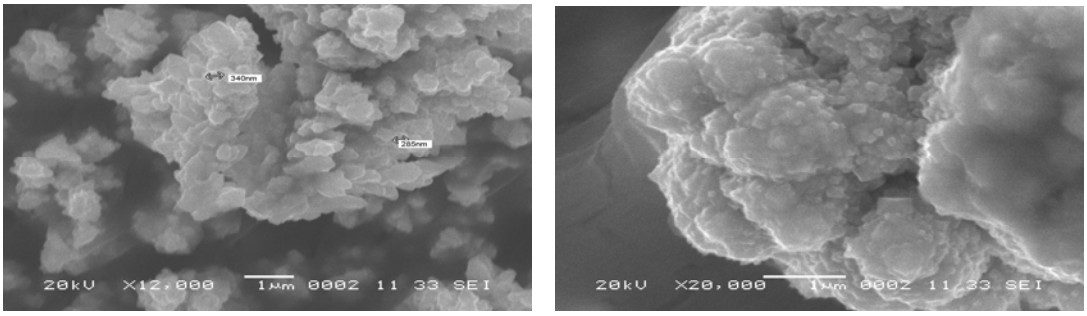
(a) (b)

Fig.3.7. SEM micrographs of Cu electrodeposit at 19.5^0C (a) silent (b) sonication

In further decrease of temperature (5^0C) the electrodeposits in fig 3.8from granular structure to somewhat like agglomerated shrub structures whereas morphology appeared in sonication are a non uniform result structures. According to the trend the deposit was expected to be full uniform agglomerated spheroids of copper electrodeposit.In both the cases a noticeable change from the micron region to nano region can be observed.



(a) (b)

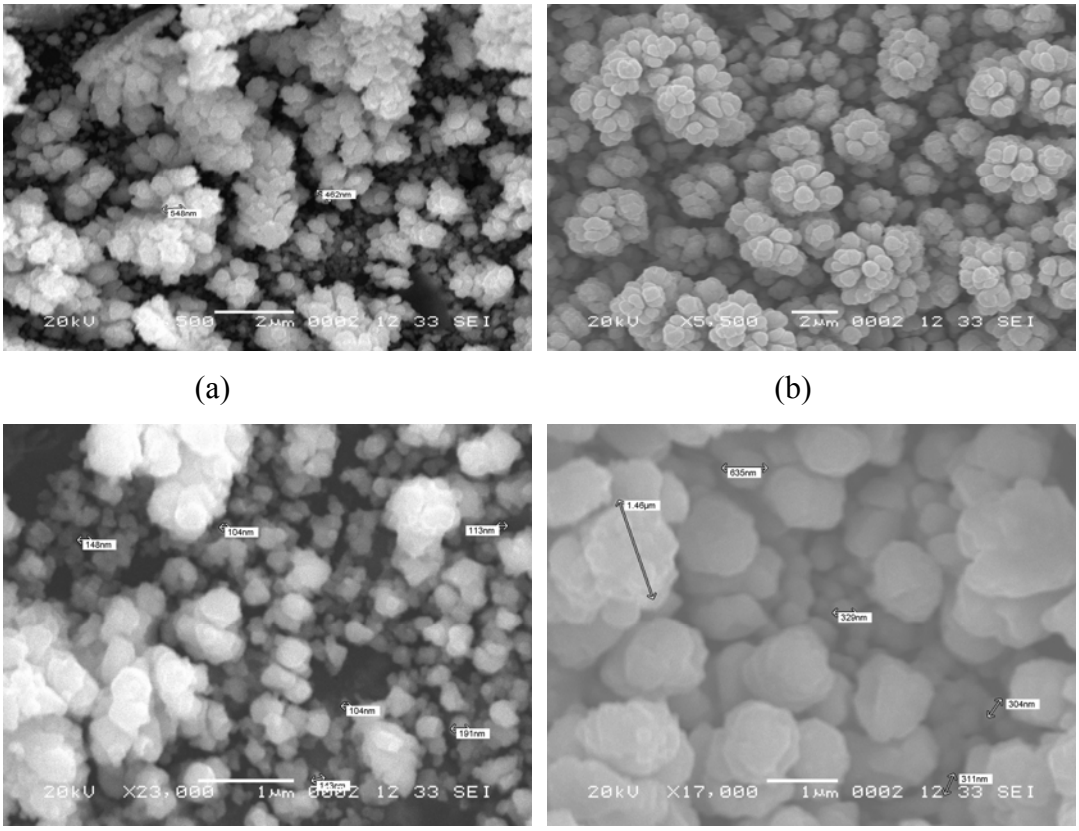


(c) (d)

Fig.3.8. SEM micrographs of Cu electrodeposit at 5^0C (a, c) silent (b, d) sonication

Temperature can affect the crystal growth in several ways, all of them resulting in a smaller crystal size at lower temperatures. The simple explanation for this is that crystal growth is slower at lower temperatures. Another temperature effect might be related to the thermodynamic instability of very small nuclei below a certain critical size. This kinetic destabilization is more effective at lower temperatures. As the temperature increases, the supersaturation decreases, which will lead to a decrease in nucleation density, and hence, the particle size increases as the temperature increases. These nuclei can redissolve, or may be thermodynamically stable, for long enough to grow larger than the critical size. This is a common mechanism to explain the decrease in colloid size with a decrease in temperature. Another additional effect that might be operative here is the presence of the heterogeneous substrate (the electrode), which can exert an additional stabilizing influence on nuclei that would be subcritical in the absence of this surface.

It can be noticed that a 3 degree decrease of temperature has resulted fully dispersed open porous agglomerated morphology (figs.3.9.) in ultrasonic irradiation as compared to a less populated corn cob like structures [48]. This discrepancy in structure may be attributed to the evolution of hydrogen bubbles under sonication. Bubble evolution was possible in irradiation is due to the localized high pressure and temperature condition resulting high mass transfer rate and decrease in overpotential with increase in temperature. According to this concept, when the hydrogen evolution is sufficiently vigorous, then the evolved hydrogen changes the hydrodynamic conditions in the near electrode layer and the obtained copper morphologies are becoming similar to the conventional copper electrodeposits



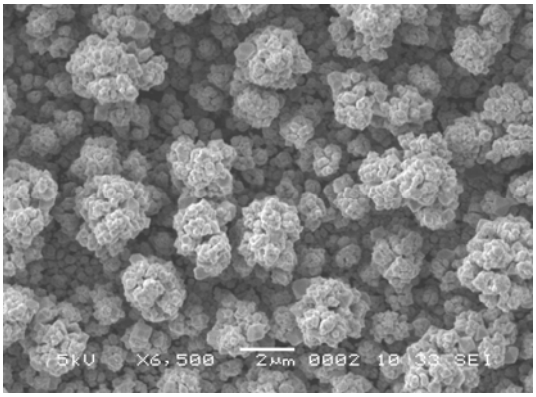
(a) (b)

(c) (d)

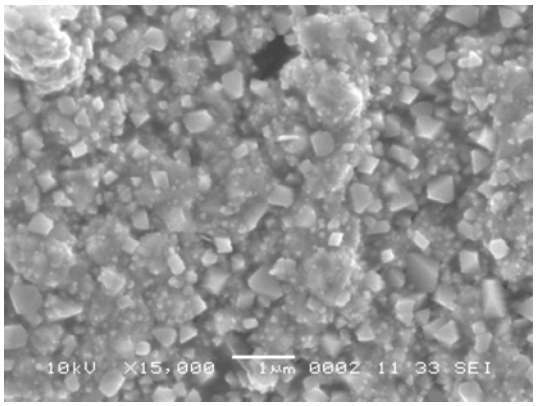
Fig.3.9. SEM micrographs of Cu electrodeposit at 3^0C (a, c) silent (b, d) sonication

An opposing effect of electrode cleaning of ultrasound may also burst the electrodeposit, but this phenomenon leads to further creation of nuclei density and clean surface for adherent and lusturious deposit. This concept was somewhat observed in the deposits at sub-ambient temperatures (-1^0C,-2^0C,-3^0C). The deposits under silent conditions (figs.3.10. a, c, e) are of not so interesting at sub-ambient temperatures (-1^0C,-2^0C, and-3^0C) but, the sonoelectrochemical deposition (figs.3.10. b, d, f) is having a very remarkable appearance at the sub-ambient temperatures (-1^0C,-2^0C and-3^0C) . The silent deposit was very much powdery and non-adherent type and sonicated deposit was fully dense, adherent, lusterious as confirmed by both the physical and microstructural analysis. The novelty of the morphology may be explained on the basis of a synergetic effect of low temperature, hydrogen evolution (due to the high degree degassing by ultrasound [49]), overpotential and high plasmon resonance of nanoparticles. A possible mechanism of the deposit may be that in the sub-ambient temperature region, mixed activation-diffusion controlled, high

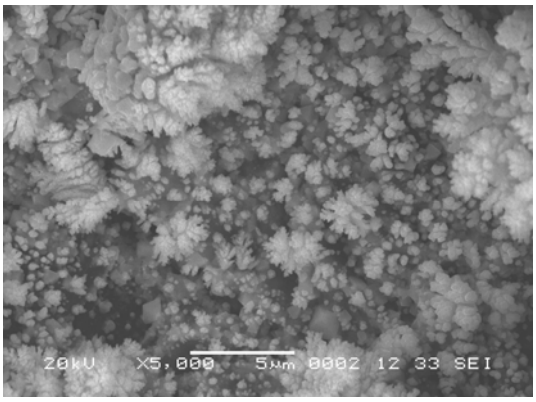
nucleation density leads a low growth rate. Due to the ultrafine particles and ultrasound, the surface melting by interparticles coalescence occurs. This leads to reduction in free energy through a reduction in free area. (e.g., agglomeration).The melting part has been described separately.



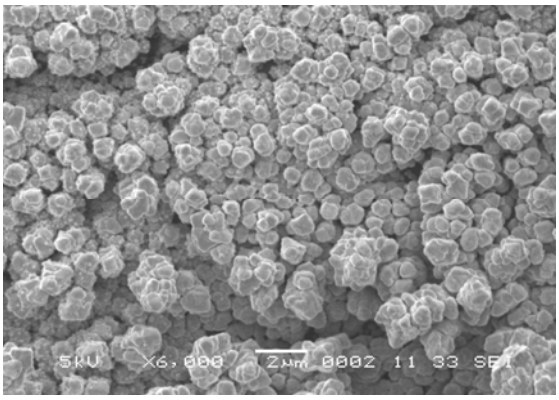
(a)



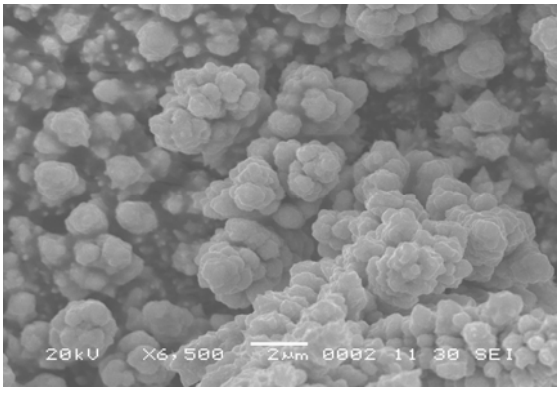
(b)



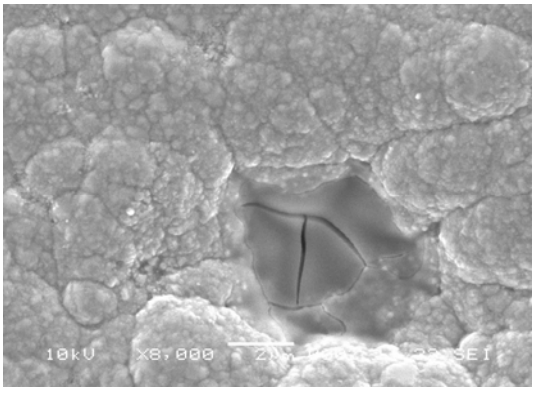
(c)



(d)



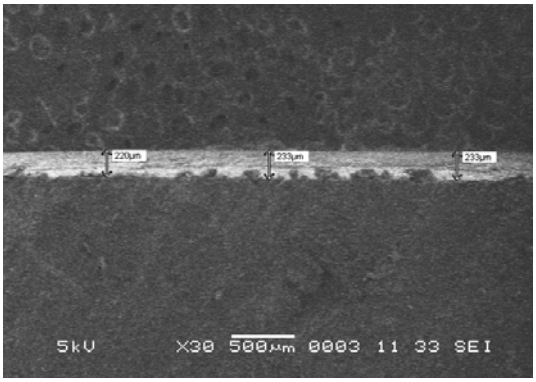
(e)



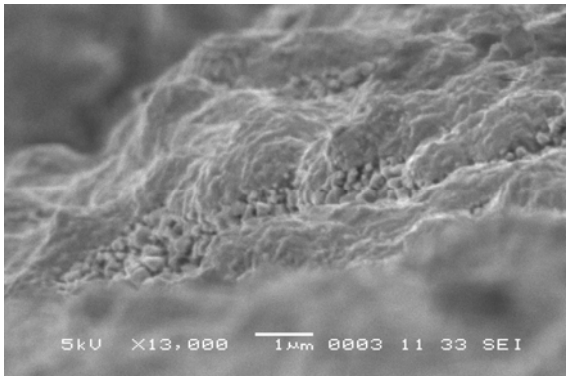
(f)

Figs.3.10. SEM micrographs of Cu electrodeposits at (-1^{0}C,-2^{0}C and -3^{0}C respectively) (a, c, e) silent (b, d, f) sonication

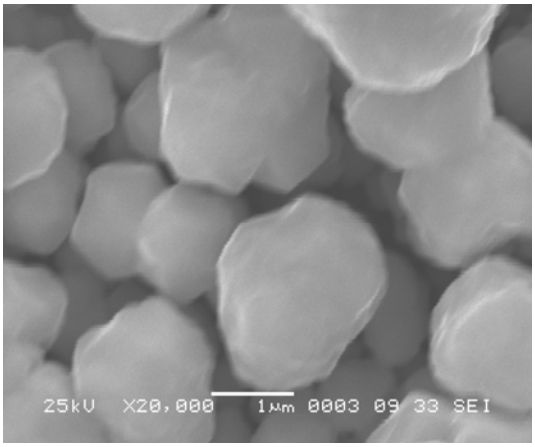
The sample was cut in the transverse direction, thickness and morphology was observed. It can be seen that the thickness is uniform (figs.3.11. a, b) and the internal structure is also well resemblance with what had been achieved at the surface. Back scattered image (fig. 3.11. d, g, h) of the ultrasound deposit shows the clusters orientation and is in close agreement with secondary electron image. The image shows that there is little mismatch between the clusters. After getting the excited results the experiments were performed for still low temperature (as much possible around -6^0C). As the experiments were performed without any antifreezer the minimum temperature attained was -6^0C.But the silent condition experiment could not be performed because of low mass transfer and requirement of high overpotential. The deposits at -4.8^0C and -5.6^0C seem to be spongy. The data is also supported by the back scattered image showing a highly diversified orientation with a broad range of size distribution.



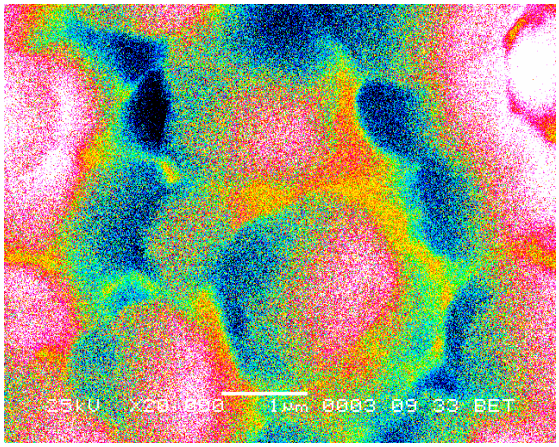
(a)



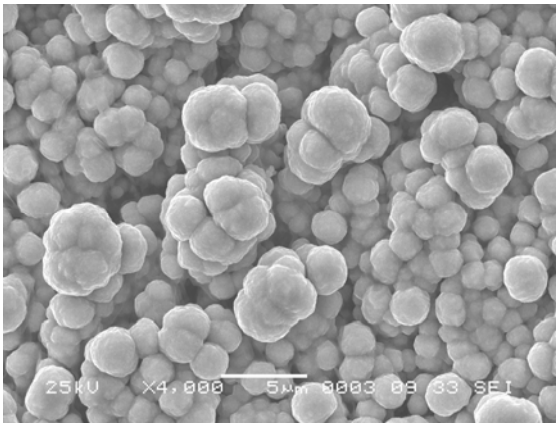
(b)



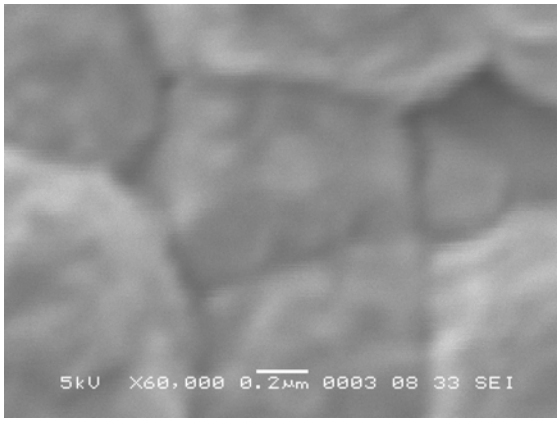
(c)



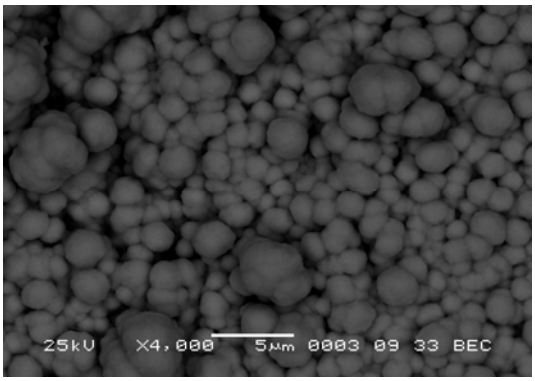
(d)



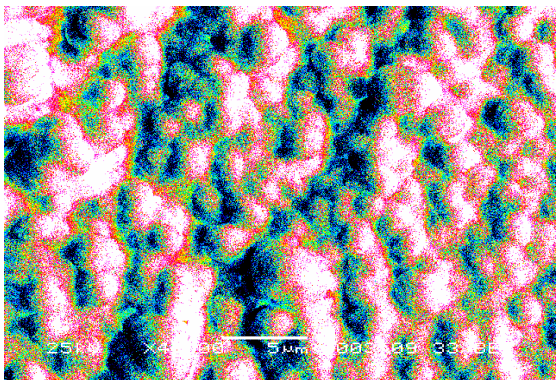
(e)



(f)



(g)



(h)

Figs.3.11. (a, b) thickness and morphology of copper sonoelectrodeposits at -3^{0}C and (d) BSI of ultrasound deposit at -4.8^{0}C (g, h) BSI of ultrasound deposit at -5.6^{0}C (c, e) SEI at -4.8^{0}C and -5.6^{0}C under sonication

3.3. PHYSICAL APPERANCE OF THE DEPOSITS

The physical appearance of the deposit can be observed from figure 3.12.

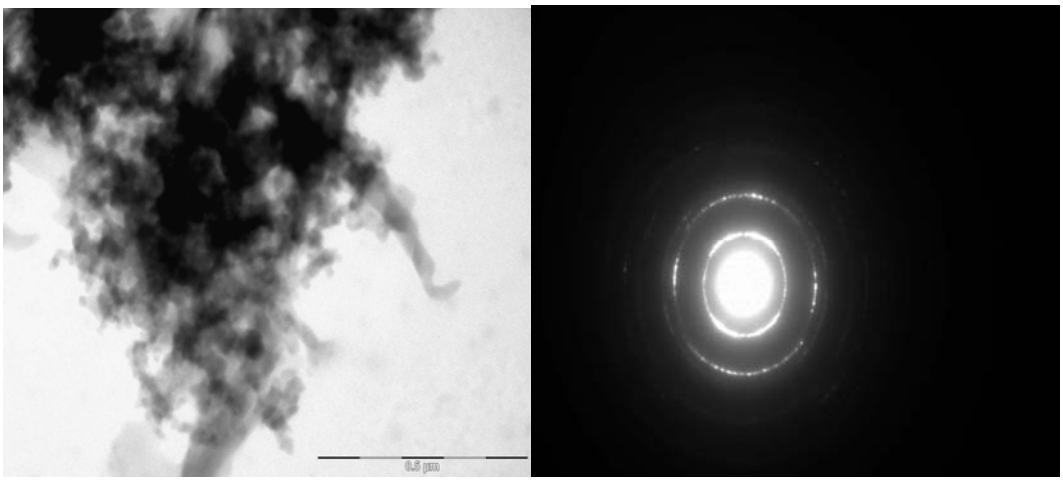
a **b** **c** **d**

fig.3.12. (a) pure copper , sonoelectrochemically deposited copper at (b) -3^{0}C , (c) -4.8^{0}C , (d) -5.6^{0}C

In the figure the deposit at -3^{0}C was compared with a pure copper plate as well as with other deposit. Figure shows the lusterious deposit at -3^{0}C as compared to the other deposits and also similar to that of pure copper plate.

3.4. **TEM ANALYSIS**

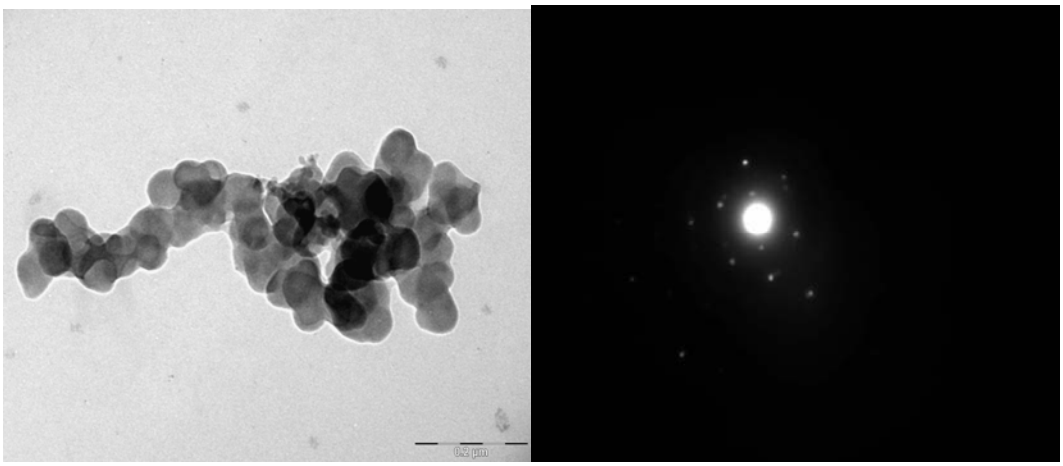
The study was done for powdered samples. The samples were vibrated for 2-3 hours in ethanol and then dried in oven at 60^{0}C for 1 hour. Then for TEM analysis it was well dispersed in ethanol and one drop of sample was put on carbon coated copper grid. Due to longer time of sample preparation and limitation in time period, this study could restrict to only two temperature ranges i.e. for 19.5^{0}C and 5^{0}C. Fig. 3.13. a & b show the bright field (BF) and selected area diffraction pattern (SADP) images of silent and sonicated samples respectively.



a b

fig.3.13. (a) BF image of electrodeposited copper at 19.5^{0}C (b) SADP of copper.

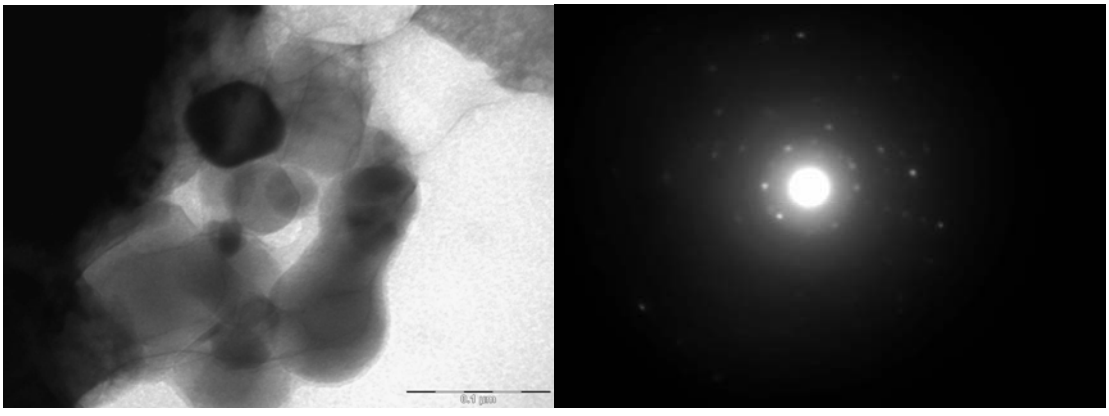
The figure shows some small equixel particles less then 10 nm and some agglomerated particles in the range of 200-400 nm. And the selected area diffraction pattern exhibits a Debye ring. This Debye ring shows fcc pattern typical to polycrystalline copper [50] and is well agreement with X-RD crystallography results.



a b

fig.3.14. (a) BF image of irradiated electrodeposit at 19.5^{0}C (b) SADP of copper.

Figure 3.14. clearly shows highly agglomerated and a great degree of neck formation due to localized melting or plastic deformation by high velocity collision under sonication treatment. The results support the result that obtained from SEM at the same temperature. Particle or cluster size lies in the range of 30-40nm. The SADP pattern shows fcc crystallinity.



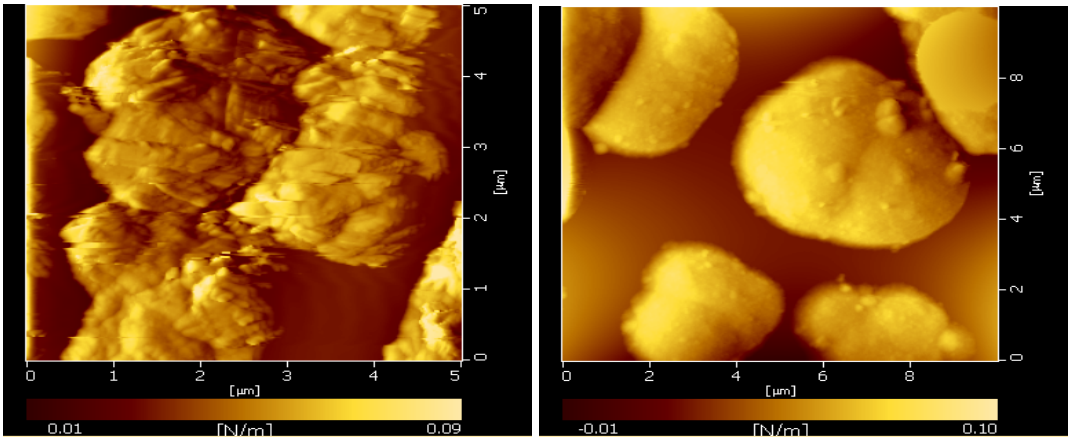
a b

fig.3.15. (a) BF image of sonicated sample at 5^{0}C , (b) SADP of the copper deposit

it can be seen from fig.3.15. that the tendency of deposit is following the same path as that of 19.5^{0}C only with a lower size regime i.e. 10-20nm and the SADP pattern also compliments the data from SEM.

3.5. AFM ANALYSIS

The sonicated deposit obtained at -3^{0}C was quite interesting and of very adherent type. To have a very in depth knowledge of the deposit and support the SEM study this study was commenced and the deposit was also compared to that of -1^{0}C

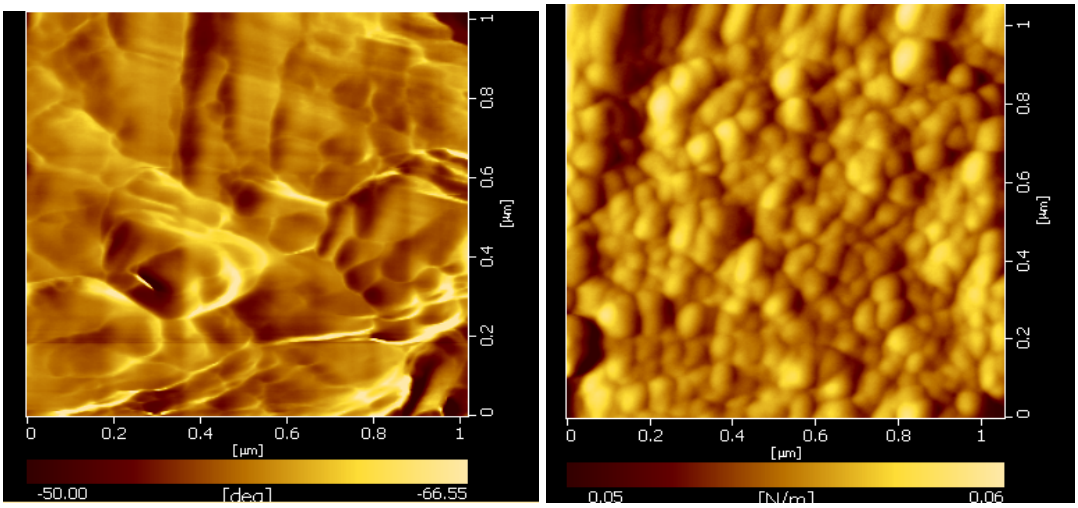


a b

fig.3.16. AFM image (a) deposit at -3^{0}C , (b) deposit at -1^{0}C

From the figure 3.16(b) it can be observed that the deposit at -1^{0}C, what appeared to be highly agglomerated in SEM seems to be a sheet of dispersed potatoes where as the deposit at

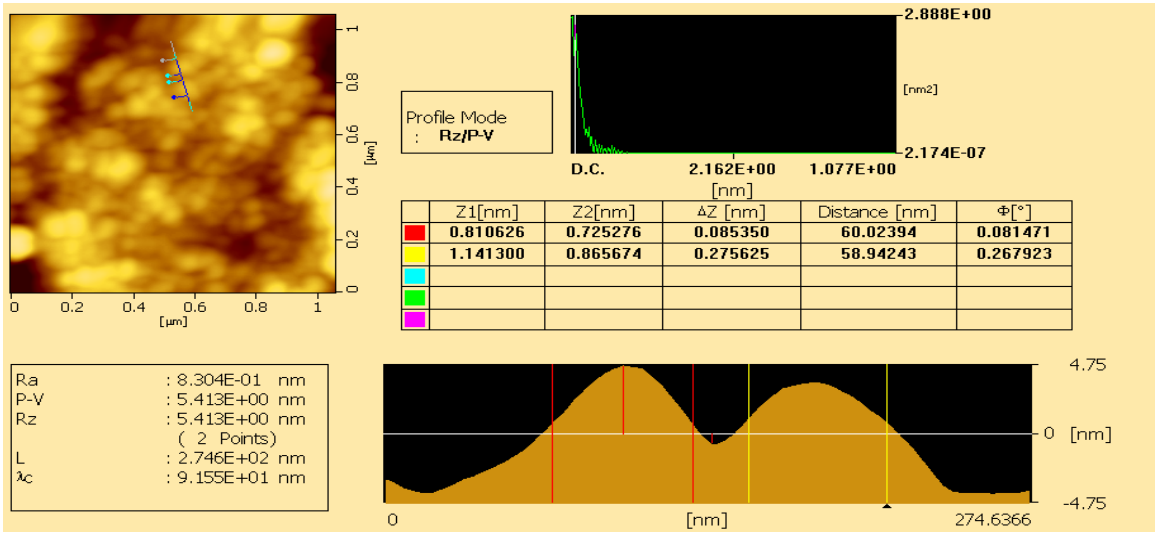
-3^{0}C is fully adherent type. Now looking closely at the deposit, fig3.17, it was found that the small globules at -1^{0}C contains large number of agglomerated particles and at -3^{0}C the figure shows no discrepancy with the counter part.



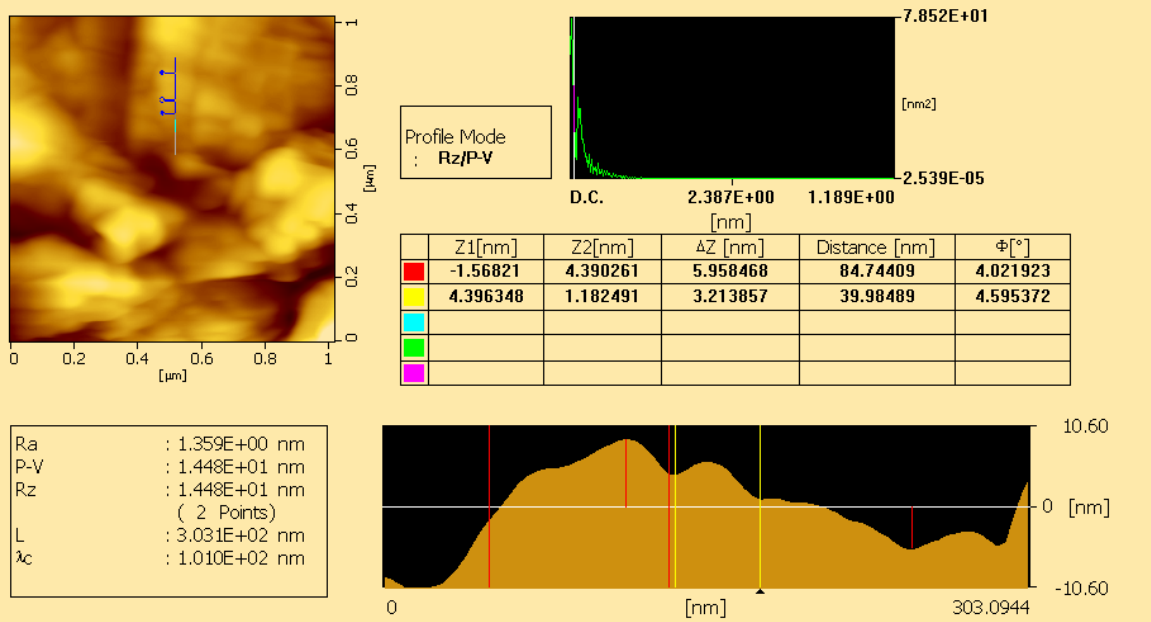
a b

fig.3.17. AFM image (a) deposit at -3^{0}C , (b) deposit at -1^{0}C

figure 3.17 shows the size range and distribution of the clusters on the surface (topographical image)



a

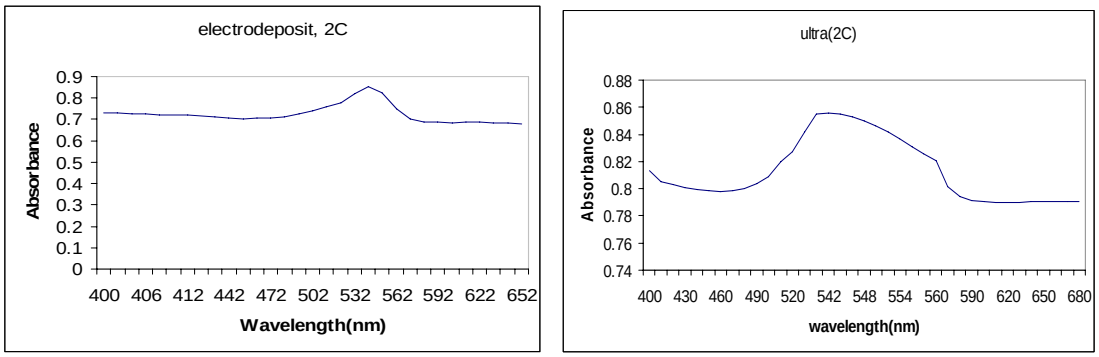


b

fig.3.18. AFM image (a) deposit at -3^{0}C, (b) deposit at -1^{0}C

3.6.UV-Vis SPECTROSCOPIC ANALYSIS

Copper dispersions of electrodeposits and sonoelectrodeposits of sub-ambient temperatures were prepared in liquid media (ethanol) where the deposits were taken out with the help of ultrasonic vibrator. The prepared copper dispersions were used for UV-vis absorption spectra. The UV-vis absorption spectra of the copper nanoparticles of sub-ambient temperatures were shown in following fig 3.22.



a **b**

Fig. 3.22. UV-Vis results electrodeposits at 2^{0}C (a) silent (b) ultrasonic

The higher intensity of the absorption band assignable to the small clusters, whereas the less intensity of the band associated with the large particles .Sonoelectrodeposits of copper shows higher intensity of the absorption band in comparison to its electrodeposits at sub-ambient temperature confirms the small cluster formation during sonoelectrochemical process at sub-ambient temperatures. A broad band peak of the absorbance spectra of sonoelectrodeposits at sub-ambient temperature shows that particles have wide size distribution than its electrodeposits at the sub-ambient temperatures. Small metal clusters were proposed to be responsible for the absorption bands in the short-wavelength range. The observed band for copper is at around 589 nm, which is due to the surface plasmon bands for the copper nanoparticles [51, 52]. It is well known that the colloidal dispersion of metals exhibits an absorption band in UV-vis regions due to collective excitations of the free electron(surface plasmon band).Sonoelectrodeposit of copper at sub-ambient temperature shows absorption band at 540 nm which is slightly lower than electrodeposit (542nm) of the copper at the sub-ambient temperature, confirms the small cluster formation during sonoelectrochemical process.

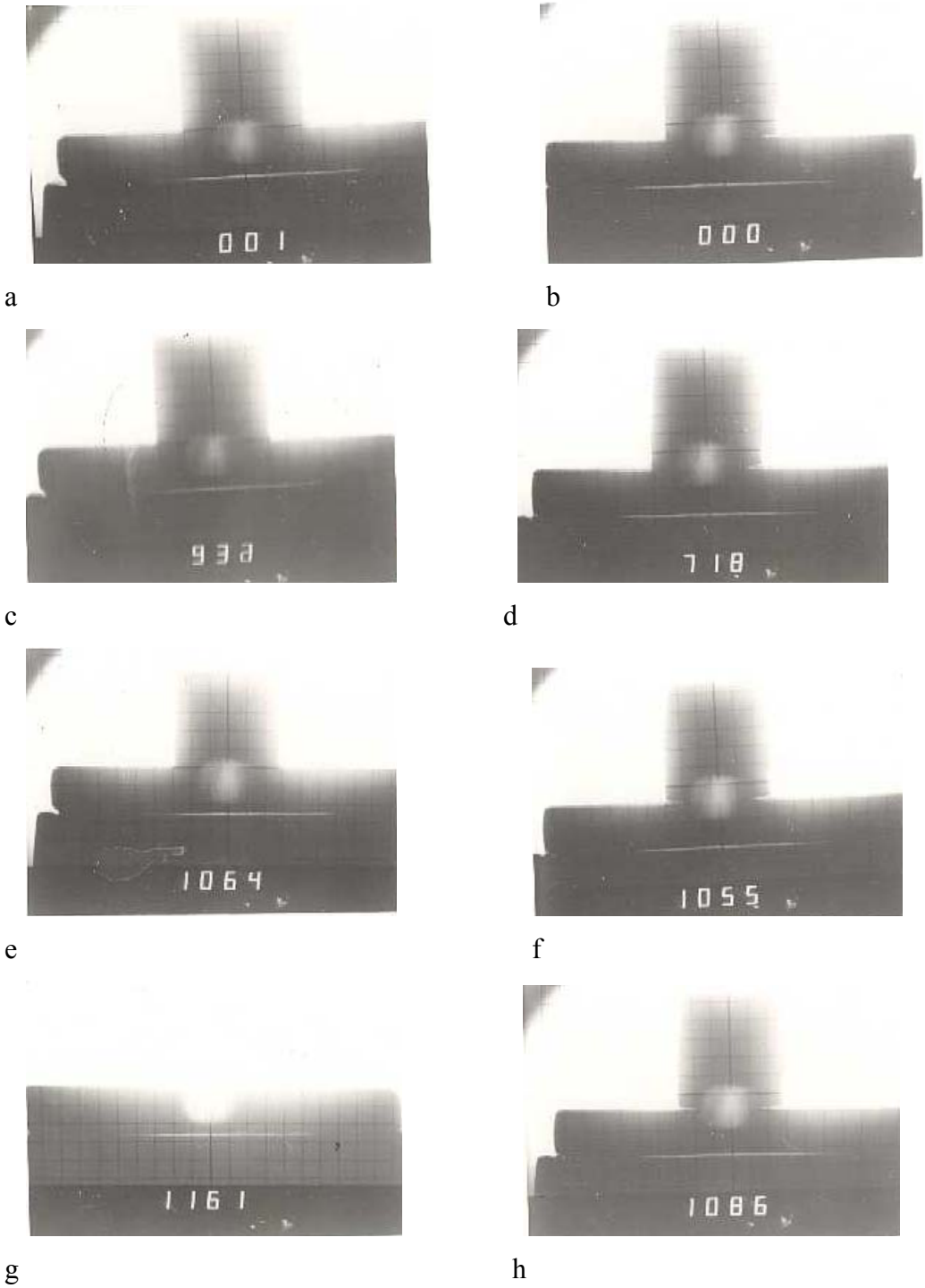
3.7. MELTING PROPERTIES OF THE DEPOSIT

With decrease of temperature coalescence of particles increases (as observed by SEM micrographs). One of the important conditions for interparticle coalescence is surface melting. The decrease in the melting point for nanosized particles is an important factor for interparticle coalescence. The decrease in the melting point with reduced particle size can be explained by the early thermodynamic model describing melting curves for fine metal particles, which relates the melting point of nanoparticles to that of its bulk metal by the equation[53]

$$\frac{T_r - T_\infty}{T_\infty} = -\frac{4}{\rho_s L 2r}\left[\gamma_s - \gamma_l\left(\frac{\rho_s}{\rho_l}\right)^{2/3}\right]$$

where T_r and T_∞ are the melting temperatures of the particle and the bulk solid, respectively, r is the radius of the particle, ρ_s and ρ_l are the densities of the solid and the liquid, respectively, ç$_s$ and ç$_l$ are the surface energies of the solid and the liquid, respectively, and L is the heat of fusion. An attempt has been made to study the above fact as shown in figure 3.23. As the deposit is in graphite substrate a minute change on softening has been observed

as that to the pellet of pure copper powder. Softening point of the deposit can be noticed at around 720^0C as compared to 900^0C of pure copper which is a bit in higher as compared to the 400-500^0C range in literature.



a b c d e f g h

fig. 3.23. heating microscope images at different stages (a, c, e, g) are pure copper and (b, d, f, h) are electrodeposited

3.8. MICROHARDNESS ANALYSIS:

Though it is a rough study for nanomaterials, it can be seen from the graph that there is a dramatic variation in hardness values at -3^0C as compared to other temperature values which is in well agreement with the Hall-Petch equation.

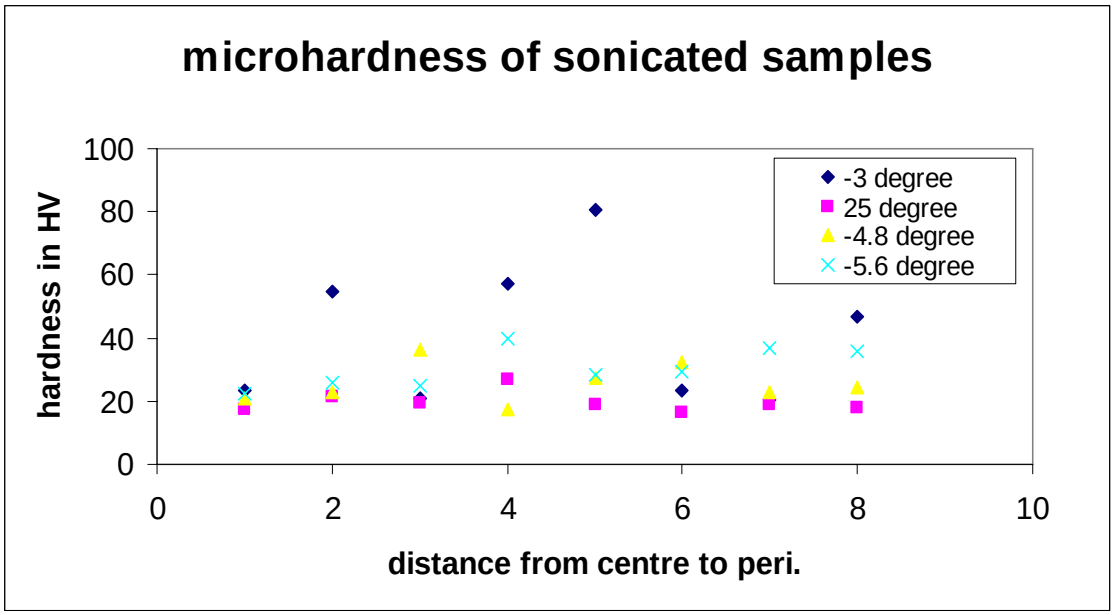


Fig. 3.24. microhardness results at (■) 25^0C (◆) -3^0C (▲) -4.8^0C (×) -5.6^0C

3.9. A POSSIBLE MECHANISM FOR THE NOVEL SONOELECTRODEPOSIT AT -3^0C:

As explained earlier the unique deposit may be due to the synergistic effect of simultaneous localized high pressure and temperature from sonication, low bath temperature, high overpotential, hydrogen evolution, high surface plasmon resonance with increasing interfacial region and tendency for reduction in surface free energy for greater stabilization. The first four phenomena strongly indicate that something has happened inside the electrolyte during deposition and the last two for conditions, though may be applicable inside the bath also, after deposition. Well to clarify the above mess an attempt has been made to study the room temperature growth by a modulated temperature differential scanning calorimeter (ADSC). The temperature setting was done at room temperature with a deflection of 1^0C to catch even a small energy daviation in terms of temperature. Figure 3.25. shows the trend after keeping the specimen for about 60hours.

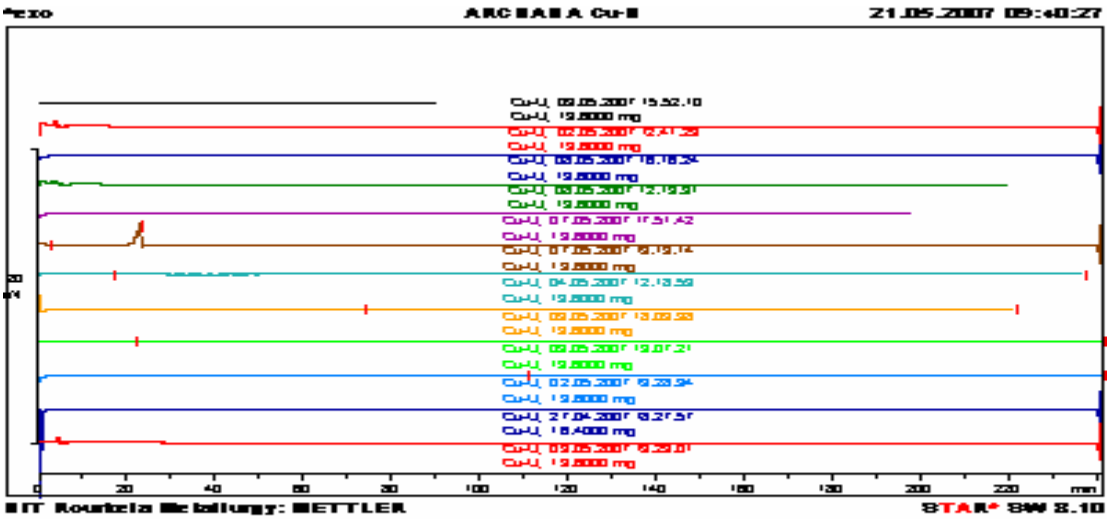


Fig.3.25. ADSC result of sonoelectrodeposited sample at -3^{0}C

It can be seen from the figure that there is hardly any change in the graph. Thus we may reach at the conclusion that, room temperature growth as proposed by various authors is restricted for nanomaterials. Then what has happened inside the solution? A possible explanation [54] may be that,

- Cu atoms dissolve from the Cu anode.
- In the solution, Cu atoms gradually collect into spheroids as they travel toward the cathode.
- At the cathode, the spheroids agglomerate under the impetus of the forces among the Cu atoms alone, without action of electric fields or chemical reactions.
- Over the minutes and hours following deposition, grain boundaries move through the assembly of spheres , so that regions up to one to a few μm are crystallographically aligned

On the basis of this observation of melting properties, it is also likely that the surface melting of the nanoparticles is responsible for the interparticle coalescence. Under such surface melting and surface tension effects, the driving force for the coalescence of two surface-melt Cu particles is the reduction in free energy through a reduction in surface area (e.g., increase in size).

Chapter 4

CONCLUSION

CHAPTER 4

4. CONCLUSION

A new route has been followed for nanodeposit formation i.e. sonoelectrodeposit at low temperature. Low temperature favors high rate of nucleation and avoids unnecessary interdiffusion. The deposit obtained was unique in terms of its morphology and properties. The electrodeposit obtained at sub-ambient temperature is porous, spongy and highly dispersed one. As has been mentioned in literature that hydrogen evolution leads to such type of deposition. Because evolved hydrogen affects the hydrodynamic condition at near electrode surface thus increasing the nucleation rate. So at low temperature gas evolution will decrease the mass transport limitation. This dispersed deposit with copper grains approaching to nanosized dimension due to the hydrogen evolution can probably be used as electrodes in many electronic devices such as fuel cells, batteries and sensors. For example, the nanoporous copper deposits are being used for construction of nanocomposite anodes [55] for solid oxide fuel cells. Now the deposit obtained under sonication approaches towards a highly adherent, dense, lusterious and sintered layer from ambient to sub-ambient temperatures. On the basis of a theoretical consideration of the size dependence of the melting temperature of copper nanoparticles, the surface melting of the nanoparticles at localized high temperature and pressure with vigorous hydrogen evolution is believed to be responsible for the interparticle coalescence leading to a novel deposit. This temperature controlled morphology yet to be established in the available open literature to the best of our knowledge. This type of structures may find their application in nanoelectronics e.g. super hydrophobic surfaces [56].

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